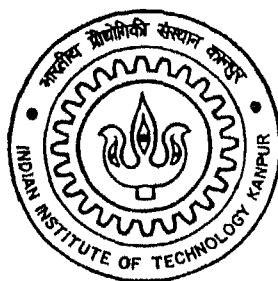


PREPARATION OF UNIFORM ZIRCONIA NANOPARTICLES AND THEIR DISPERSION IN A SILICA FILM

By

SUDIP DASGUPTA



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MATERIALS SCIENCE PROGRAMME

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

DECEMBER 2003

**PREPARATION OF UNIFORM ZIRCONIA
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SILICA FILM**

*A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of*

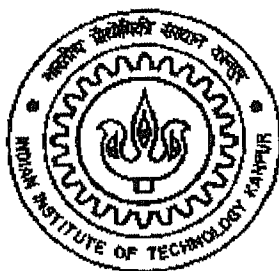
MASTER OF TECHNOLOGY

In

MATERIALS SCIENCE

By

SUDIP DASGUPTA



**MATERIALS SCIENCE PROGRAMME
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
DECEMBER, 2003**

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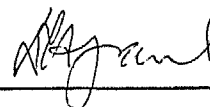
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CERTIFICATE

It is certified that the work contained in the thesis entitled *Preparation of uniform zirconia nanoparticles and their dispersion in a silica film* by Mr Sudip Dasgupta (Roll No Y121206) has been carried out under my supervision and that this work has not been submitted elsewhere for any degree

24 December 2003



Dr D C Agrawal

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DEDICATED
TO
MY PARENTS

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ABSTRACT

Ceramics with nanosized grains possess exceptional chemical, mechanical and electrical properties. Although several methods have been reported in the literature for preparation of monodispersed nanosized zirconia powders, but wet chemical routes via hydrolysis of aqueous solution of the metal salt have been found to be the simplest.

In the present study, both undoped and Gd_2O_3 doped nanoparticles of hydrous zirconia with a narrow size distribution have been prepared by microwave heating of aqueous solution of zirconyl chloride isopropanol mixture using hydroxypropyl cellulose (HPC) as a surfactant. TEM micrographs reveal that hydrous zirconia particles in the size range of 35 nm to 150 nm can be prepared as $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration is varied from 0.01 M to 0.05 M at a fixed HPC concentration of 1.71×10^{-3} gm/cc. Particle size for doped and undoped zirconia powder does not vary too much in the same precursor concentration range. 10 mol% Gd_2O_3 doped ZrO_2 powder with very high surface area ($\sim 300 \text{ m}^2/\text{gm}$) has been prepared by using a $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration of 0.01 M.

Hydrous zirconia particles with narrower size distribution have been prepared by a two-step heat treatment under controlled condition. A microwave treatment at 80% power for a few seconds followed by aging at 50°C for 8 hours seem to be the optimum conditions for obtaining hydrous zirconia particles with narrow size distribution (15 nm width at half maximum).

The variation in zeta potential of 10 mol% Gd_2O_3 doped zirconia powder was measured as a function of pH and the isoelectric point of the powder was found to be 4.8. The surface properties of zirconia nano particles were modified by coating with a second phase using sol gel technique. Time dependent growth of a silica layer on zirconia particles suspended in a TEOS sol at pH 3.5 has been measured by observing the changes in zeta potential of the zirconia particle with respect to time. The zeta potential is positive in the beginning and becomes negative after aging for some time.

Dispersion of second phase (ZrO_2 - Al_2O_3) particles in thick sol gel films has been effected by the use of a surfactant. It has been possible to disperse the particles uniformly in the film under certain conditions. Dispersion of second phase particles effectively prevents the cracking of those films. It has not been possible to correlate the arrangement of the particles within the film with the processing condition so far.

The crystallization of the as prepared amorphous hydrous zirconia particles is studied by calcination at 600°C and 900°C respectively. The undoped crystallized powders prepared from lower precursor ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) concentration show only cubic phase whereas the powders with higher particle size prepared from higher amount of precursor concentration show a mixture of cubic and monoclinic phase at 600°C . However for Gd_2O_3 doped powder it is only the cubic phase that exists in the crystallized powders in the temperature range from 600°C to 900°C and the crystallite size proved to be independent of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration.

CHAPTER 1

INTRODUCTION

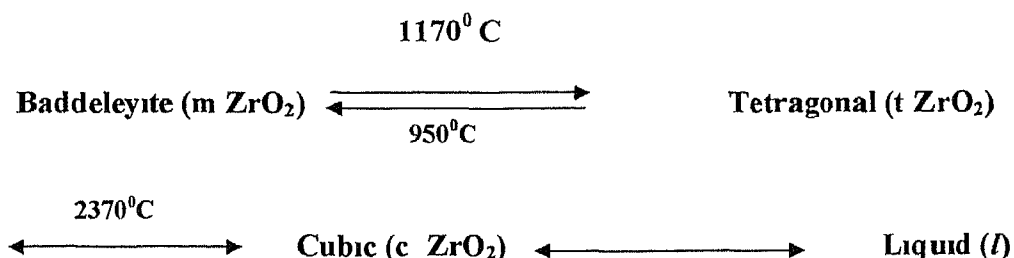
1 1 Importance of Nano Ceramics

Nanocrystalline ceramics are known to be very promising materials which exhibit dramatic changes in properties due to a high interfacial area with respect to their coarse grained counterparts. These properties are for example excellent sinterability and formability, enhanced diffusion and ion conductivity at moderate temperatures etc. By using nano particles the sintering temperature can be lowered by several hundred degrees and the use of sintering aids can be avoided. Problems such as decomposition of constituent phases that are frequently encountered in sintering of nitrides and deleterious interfacial interactions can be solved by resorting to nano particles as starting materials. Smaller grain size in nanometer range should result in improved mechanical properties and superplastic behavior for net shape forming.

1 2 Zirconia General

Zirconia is one of the most important ceramic materials. The unique chemical, mechanical and electronic properties of zirconia ceramics have led to their widespread use as structural materials, solid state electrolytes, thermal barrier coatings, oxygen sensors, catalyst supports, corrosive coatings and as inclusion in composites for increasing toughness. These properties change with crystallite size, especially when it is of the order of nanometer. With these dimensions, zirconia can also be used as a ceramic binder at high temperatures or as a self-lubricating material in sliding.

Zirconium dioxide (zirconia) has three allotropes monoclinic tetragonal and cubic It exhibits phase transformations as follows



During cooling the tetragonal phase (t) transforms diffusionlessly to a metastable monoclinic phase (m) at the martensitic temperature ($T_0^{t \rightarrow m} \sim 950^{\circ}\text{C}$) On heating the m phase changes to t phase at the austenite temperature ($T_0^{m \rightarrow t} \sim 1170^{\circ}\text{C}$) diffusionlessly with no compositional changes The displacive phase transformation from t ZrO_2 to m ZrO_2 accompanied by 4–6% volume increase and 1–2% shear strain renders pure ZrO_2 unsuitable for engineering use The transformation from the tetragonal to the monoclinic (t \rightarrow m) phase of zirconia is known to be a martensitic transformation The transformation occurring in ceramics containing tetragonal zirconia greatly enhances their toughness

Stabilizers are essential for retaining the tetragonal phase with at room temperature Aliovalent oxides such as R_2O_3 (R= Y Gd Nd Sc etc) CaO MgO CeO_2 are effective stabilizers which when added to ZrO_2 stabilize the tetragonal and cubic phases of ZrO_2

Depending on their microstructure the ceramics containing t-zirconia are mainly classified into three groups tetragonal zirconia polycrystals (TZP) partially stabilized zirconia (PSZ) zirconia toughened ceramics (ZTC) TZP such as CeO_2 stabilized tetragonal zirconia polycrystals usually show a microstructure of homogeneous tetragonal grains The PSZ such as such as Mg – PSZ Ca PSZ consist of

relatively large grains of cubic ZrO₂ containing coherent submicrometre sized tetragonal precipitate. In ZTC + ZrO₂ particles are dispersed in second phase e.g. Al₂O₃ (ZTA).

Monoclinic ZrO₂ has Zr⁴⁺ ions coordinated with seven oxygen ions which after substitution by other aliovalent oxides causes the creation of oxygen vacancies in order to maintain the overall charge neutrality. This reduces the internal strain leading to the stabilization of the cubic fluorite structure of zirconia. The addition of 10 mol% or more Gd₂O₃ in ZrO₂ results in formation of the fluorite phase. This structure contains metal ions at the body centres and face centres and the oxygen ions occupy the eight tetrahedral voids as seen in the figure 1.1.

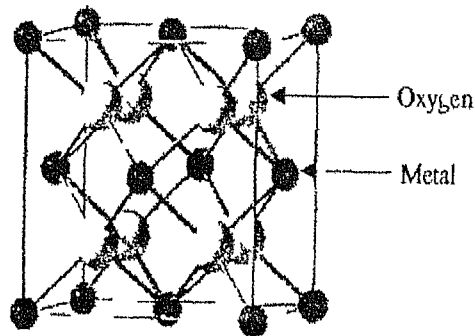


Figure 1.1 Fluorite crystal structure of ZrO₂

1 3 Importance and applications of nanocrystalline zirconia

Because of the very fine grain sizes nanocrystalline zirconia exhibit a variety of properties that are different and considerably improved in comparison with those of conventional coarse grained zirconia. Some of the advantages are given below

- i) Diffusivity and sinterability are expected to be enhanced in comparison with coarse grained crystalline zirconia
- ii) The electrical, optical and chemical properties are superior than in the conventional coarse grained structure
- iii) Due to its fine grain size it has an improved forming characteristic which is an advantage over coarse grained structure
- iv) Improved mechanical properties and increased wear resistance
- v) Better physical optical properties due to enhanced control over fine particles

1 4 Synthesis routes of Nanocrystalline zirconia powders

1 4 1 Mechanically activated exchange reaction

Ultrafine powders of very high quality can be synthesized by mechanically activated exchange reactions. In this process chemical precursors undergo reaction either during milling or during subsequent low temperature heat treatment to form nanocrystalline particles embedded within a salt matrix. The ultrafine powder is then recovered by removing the salt through a simple washing procedure. This technique has successfully been used to synthesize a wide variety of materials including transition metals, magnetic intermetallics, sulfide semiconductors and oxide ceramics.

The characteristics of the final washed powder can be significantly controlled by mechanochemical synthesis technique. For example, the average particle size can readily be controlled through the use of inert diluents and post milling heat treatments. By solid state reaction¹ at 500°C tetragonal zirconia of crystallite size 9 to 25 nm was prepared. In their work Dodd and McCormick¹ used anhydrous zirconium chloride ($ZrCl_4$) and Li_2O reactant mixtures (1:2 mole proportion) which were milled for 6 hrs within a hardened steel vial using a Spex 8000 mixer/mill. All millings used a 10 g powder charge with 20 9.5 mm stainless steel balls as the grinding media. To ensure an inert atmosphere during milling, the grinding media and reactants were loaded into the vial whilst within a high purity argon filled glovebox. Following milling, the reactant mixtures were heat treated at 400°C for 1 hr under a sealed argon atmosphere. To remove the Li_2O by product phase, the heat treated powders were washed several times with deionized water and methanol in an ultrasonic bath. Following each wash, the powder was recovered from the solvent by means of centrifugation and decantation. Washed powders were subsequently dried for several hours in air at approximately 80 °C.

1.4.2 Powder preparation by sol gel method

The sol gel method using alkoxides as precursor materials is a very popular approach for preparation of monodispersed ceramic powder. Srutt et al.² reported the sol gel derived nano structured tetragonal zirconia using zirconium n-butoxide as precursor and HCl , CH_3COOH and NH_4OH as hydrolysis catalysts. To study the effect of tetragonal phase stabilizer, nanocrystalline tetragonal zirconia stabilized with yttrium was also prepared via the hydrolysis of an aqueous solution of zirconyl and yttrium chlorides, yttrium concentration being 5.0 mol%.

When samples were annealed at 400°C they crystallized. The sample without yttrium was a mixture of nano crystalline monoclinic zirconia (82 wt %) and tetragonal zirconia (18 wt%) with an average crystallite size of 19.9 nm. On the other hand the yttria doped sample only had nanocrystalline tetragonal zirconia with an average crystallite size 12.2 nm.

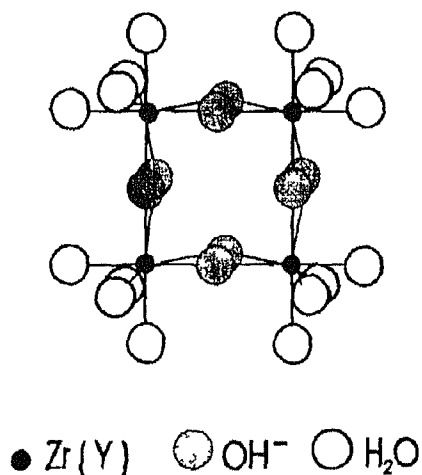


Figure 1.2 Structure of hydrous zirconia produced by sol-gel technique

The zirconia samples prepared by the sol-gel technique were amorphous when heated below 300°C. This occurred because the zirconyl group has 16 aquo bindings at which condensation randomly occurs, preventing crystallization. When samples were heated at higher temperatures, the hydroxo bridges between zirconium atoms were transformed, causing the system to stabilize into the tetragonal zirconia nanophase.

During sample preparation, the ions present in the synthesis were hydroxyls, *n*-butoxyl, Cl⁻, methyl, carboxyls, and ammonium. The carbon and hydrogen atoms present in methyl and *n*-butoxyl groups require a lot of energy to substitute for oxygen in the crystalline structure of zirconia and therefore they are discarded to stabilize the

tetragonal structure. For Cl⁻ ions to substitute for oxygen atoms or to form chlorate ions also requires too much energy and thus they can not play any role as tetragonal phase stabilizers. Nitrogen atom originating from ammonium ions can also not substitute for oxygen at this low synthesis temperature to stabilize the tetragonal phase.

The only group having oxygen atoms that could occupy sites in the crystalline structure of zirconia are hydroxyl and carboxyls. Since hydroxyls were present in both yttria doped and undoped powders, it can be assumed they stabilized the tetragonal structure. When samples were annealed at 600^o C at which they were strongly decarboxylated, the tetragonal phase was only stable in the sample prepared with acetic acid hydrolysis catalyst. This implied that carboxyl group also stabilized the structure.

Wang et al.³ also studied the sol-gel method by dissolving zirconium *n*-butoxide in absolute ethanol under continuous stirring and then adding hydrolysis agent (NH₄OH) till pH became ~10. After that a small amount of water was added and the solution was stirred continuously until gelling. The gel was subsequently dried at room temperature in a vacuum for 24 hours. Then these gel powders were subjected to annealing at 400^o, 600^o and 800^oC for 4 hours in air. Nanocrystalline zirconia with coexisting monoclinic and tetragonal phases with an average crystallite size ranging from 6 to 36nm was obtained. They have also found that the fractions of the phases change with annealing temperature. At 400^oC the main phase was tetragonal. But when temperature was increased from 400^o to 800^oC the tetragonal fraction decreased (from 84 to 11.9 wt%) while the monoclinic phase concentration increased (more than 80 wt% at 800^oC). This synthesis method leads to formation of t and m phase without cubic phase and irreversible phase transformation from t → m occurs during calcination. This is in contrast with the result obtained by

Yoshimura M^4 where transformation of low temperature m phase to the t phase and then into cubic phase at higher temperature was reported. In all these investigations the nanocrystallites are agglomerated into large particles (> 100 nm). So the preparation of particles with size < 100 nm is still not so easy using the sol-gel method.

1.4.3 Citrate–nitrate combustion route

Gel combustion methods show some advantages due mainly to its relatively low cost compared to alkoxide based sol-gel methods and better control of stoichiometry in comparison with co-precipitation ones. Gel combustion routes are based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals (usually nitrates) and some organic fuel such as urea and carbonylhydrazide and oxalic dihydrazide, citric acid and glycine and alanine etc. The combustion process is due to an exothermic redox reaction between nitrate ions and the fuel. The large volume of gases produced during the reaction promotes the disintegration of the precursor gel yielding nanocrystalline particles after calcination.

Juarez et al.⁵ studied the synthesis of zirconia nano powder by dissolving zirconium oxychloride and yttrium oxide in an excess of nitric acid in a ratio corresponding to a final composition of ZrO_2 2.8 mol% Y_2O_3 . This nitrate solution was thermally concentrated in order to eliminate chlorine. Citric acid was then mixed in a proportion of 2 mols per mol of metal atom and the pH of the solution was adjusted to pH=7 by adding ammonium hydroxide. The resulting translucent solution was heated on a hot plate (at about 200 ± 250 °C) until it turned into a black viscous gel and then burnt due to a vigorous exothermic reaction. The system was homogeneous during the whole process and no precipitation was observed. Grey ashes obtained after combustion were treated at

350⁰ C in air for 1 h to eliminate the carbonaceous residues and calcined at 600⁰C for 2 h resulting in a white foamy powder. It was then milled at 110 rpm in a non contaminating plastic container with zirconia pellets in an ethanol medium. The as synthesized powder exhibited the tetragonal phase at room temperature because of their small crystallite size (about 10 nm) while the milled powder presented a small amount of the monoclinic phase (a volume fraction of about 20%)

1.4.4 Preparation of Nano powder from a polymeric precursor

There are various techniques for the preparation of nano particles. Of these pyrolysis of polymeric precursor is one of the simplest methods for the production of fine grained oxide powder.

In their work Pramanik⁶ et al. used zirconium oxychloride as a precursor by dissolving it in a minimum quantity of distilled water. From this solution zirconium hydroxide was precipitated by the addition of ammonium hydroxide. The precipitate was washed several times to remove Cl⁻. Then the precursor nitrate solution was prepared by the reaction of nitric acid and hydroxide. To prepare pure zirconia, a predetermined proportion of sucrose and PVA were added to the nitrate solution and the resulting mixture was evaporated to a viscose mixture on a water bath to avoid frothing in subsequent heat treatment. Then the mixture was heated on a hot plate to about 200⁰C to make a black porous mass and in some cases a white powder was obtained for uniform heating. This mass was ground to powder for calcination. The resulting powder was calcined at various temperatures to make the nano crystallites of pure zirconia.

To prepare yttria stabilized zirconia yttria was dissolved in nitric acid to form a yttrium nitrate solution which was mixed with zirconium nitrate solution in the proper proportion. The resulting solution was mixed with sucrose and PVA.

For preparation of YSZ the same ratio of sucrose and metal ion as before was used. The pyrolysis and the calcination temperatures are 200 300 400 600 700 800 1000 and 1200 °C and the time used in each case is 2 h except for 200 °C where the time used is 6 hr.

It was observed that small amount of sugar was not sufficient for making nanophase material. Addition of excess sugar introduced a problem in the removal of carbon from the material which required higher temperature and longer time. This facilitated the growth of the nano crystallites. Hence the optimum amount of sugar was essential. In both cases pure zirconia and YSZ the optimum ratio of the metal ion and sucrose was 1:4.

In another work Pramanik et al.⁷ reported the synthesis of Cr³⁺/Cr⁴⁺ stabilized c-ZrO₂ nano crystals using metal cations in a solution of sucrose and polyvinyl alcohol (PVA). White gelatinous precipitate of Zr(OH)₄·xH₂O was obtained by the reaction of ZrOCl₂·8H₂O and NH₄OH in aqueous solution. Zr(OH)₄·xH₂O was dissolved in nitric acid to form solution of ZrO(NO₃)₂ and Cr⁶⁺ cations were added through a 1 (M) aqueous (NH₄)₂Cr₂O₇ solution. Addition of sucrose and PVA (mol wt 125 000) by 50–70% by weight in a batch of 20 g sample yielded a final precursor solution in a transparent light green color. The molar ratio of sucrose and PVA monomer was about 10:1. The solution was dried over a water bath into a precursor mass of a dark black color. The latter was pyrolyzed on a hot plate at 250°C to give a fluffy powder having light brown to deep blue color as per Cr (atomic percent of chromium cations) content in the sample. Calcinations

at 600–900°C resulted in a stabilized ZrO₂ nano powder. A series of samples with Cr content up to 30 at% have thus been obtained after calcining at different temperatures.

Sucrose and PVA forms a polymer with dissolved metal cations in water. Here sucrose plays a multifunctional role. At first, it forms a complex with metal cations by coordinating through hydroxyl groups. It prevents selective precipitation of coordinating cations while evaporating the excess water in the solution to a dried precursor mass.

Robert et al.⁸ in their work reported YSZ powder preparation via polymeric precursors made from citric acid and ethylene glycol. In this process, an alpha hydroxycarboxylic acid (citric acid) was used to chelate with various cationic precursors by forming a polybasic acid. In the presence of a polyhydroxyl alcohol (ethylene glycol), these chelate reacted with it to form organic esters and water by products. When the mixture was heated, polyesterification occurred and led to a homogeneous sol in which metal ions were uniformly distributed throughout the organic matrix. When the sol was further heated to remove the excess of solvents, an intermediate resin was formed. The solid resin was then heated to elevated temperatures to remove organic residuals and the desired stoichiometric compounds were formed during the pyrolysis.

Panda and Pramanik⁹ studied the stabilization of the metastable states of ZrO₂ with tetravalent cation Th⁴⁺ or Ti⁴⁺ using zirconium oxychloride (ZrOCl₂ · 8H₂O), thorium nitrate [Th (NO₃)₄], titanium oxide, tartaric acid, hydrofluoric acid, and Triethanolamine (TEA) as starting materials. At first, zirconium oxychloride was converted into zirconyl nitrate solution via zirconyl hydroxide and mixed with thorium nitrate solution with proper mole ratio to form 1.0, 2.5, 5.0, 10.0 at. % Th⁴⁺ containing ZrO₂ in the final product. With the above mixed solution, 6 M TEA was added per mole of total metal ion.

to form the precursor solution. In the similar way Ti^{4+} containing precursor solution is prepared. In this case Ti^{4+} was introduced into the precursor solution as its tartarate which was synthesized chemically.

Then the precursor solutions were evaporated and pyrolyzed over a hot plate for about 4 hrs at a bed temperature of 250°C to form the precursor material. These are calcined at different temperatures ($650\text{--}1200^\circ\text{C}$) to form the nanocrystalline powders.

At the calcination temperature of 650°C t-ZrO_2 with the average crystallite size of 10 nm was reported. Beyond 950°C t-ZrO_2 started transforming into m phase and at 1200°C complete transformation occurred. The average crystallite sizes at these temperatures are 20 and 35 nm respectively. The result showed that lower concentration of Th^{4+} also can stabilize the t-ZrO_2 but its thermal stability is lower than the tetragonal phase containing 5 mol% Th^{4+} . Even 1 mol% Th^{4+} can stabilize t-ZrO_2 . However, higher concentration of Th^{4+} did not improve the thermal stability of t phase. Therefore 5 mol% Th^{4+} is the optimum composition for the stabilization. Stabilization characteristics of t-ZrO_2 using Ti^{4+} is almost similar to except the lower thermal stability. At the calcination temperature of 1000°C total transformation into m phase occurred in case of Ti^{4+} stabilized t-ZrO_2 . At 900°C about 8% m phase appeared for the 5 mol% Th^{4+} stabilized sample but in the case of 5 mol% Ti^{4+} stabilized sample it was only about 3% m phase is present even at the calcination temperature of 950°C . Therefore it can be concluded that the stabilizing ability of Th^{4+} is better than Ti^{4+} with respect thermal stability.

The cationic radius of Th^{4+} (0.95 Å) is greater than Ti^{4+} (0.64 Å) which is probably the reason of different stabilizing ability. Ionicity of Th^{4+} and Ti^{4+} is not very different, so it may not play an important role for making any difference in ability of

stabilization. This proves the dopant size effect for stabilization. The stabilization of t ZrO_2 with ThO_2 is similar to effect with SiO_2 as reported by del Monte et al (ref 10) and superior to the stabilization of t ZrO_2 with SnO_2 as reported by Ray et al (ref 11). Here again ionic charges of Si^{4+} , Sn^{4+} and Th^{4+} are same. The effect of Si^{4+} will be different from the other because of its higher covalent character of the Si–O bond. In general it shows that with an increase of size of ion the stabilization effect from metal ion increases.

1.4.5 Laser ablation

W. Riehemann et al.¹⁰ has reported the generation of solid solution of the nanoparticle system $\text{Al}_2\text{O}_3\text{-ZrO}_2$ by evaporating a blend of Al_2O_3 ZrO_2 micro powders with the pulsed radiation of a Nd:YAG laser followed by condensation of the induced vapor in a controlled atmosphere. The advantage of this laser method is that a large magnitude of micro powder mixture can be used for ablation, enables the generation of new material phases of the constituent which are additionally free from contamination as e.g. solvents or other residuals.

1.4.6 Inert gas Condensation Process

By the gas condensation method (originally proposed by Gleiter) nano structured monoclinic zirconia particles (dia. ranging from 4 to 8 nm) have been synthesized and at high pressure tetragonal structure is obtained depending on size.

G. Skandan et al.¹¹ has studied the nanoparticle preparation by inert gas condensation technique. They evaporated zirconium monoxide nanoparticles in an ultra high pure helium atmosphere of 2–20 mbar. Evaporation of the monoxide rather than the metal is common and advantageous since greater control could be exercised in the post deposition oxidation step. This is because the exotherm generated in converting a

monoxide to its oxide is much less than that generated on going from a metal to its oxide. The average particle size principally depends on the He gas pressure during evaporation. Particle size as determined from the bright field TEM images increases from 6 nm to 12 nm at 2.75 to 20 mbar pressure respectively. The measured surface area for the finest nano zirconia powder was 136 m²/gm.

1.4.7 Pyrolysis

Pyrolysis of the precursor is one of the most common and convenient processes for the synthesis of nano particles of zirconia.

1.4.7.1 Spray Pyrolysis

Chuanxian Ding et al.¹² reported the synthesis of zirconia nano particles (50–120 nm in diameter) by this technique by spraying dried granules of ZrO₂–3mol% yttria in the range of 15–40 mm into distilled water and depositing onto stainless steel substrates located at 120 mm away from the plasma gun nozzle. The Ar–12% H₂ mixture was used as plasma forming gas. Prior to the spraying, the substrate was degreased ultrasonically in acetone and blasted with alumina grit. During spraying, the substrates and coatings were cooled using compressed air.

By spray pyrolysis¹³ of an aqueous solution of zirconium acetate, the process at 550°C yields pure zirconia in the cubic phase and at 1000°C it forms only the monoclinic phase via a small amount of tetragonal phase. At 500°C YSZ forms the cubic phase and maintains this form as a major phase up to 1000°C.

In the plasma based ultrafine particle synthesis process (PSP) the following steps are followed in a sequential manner:

- (i) Liquid droplet is atomized and injected into the plasma flame
- (ii) The plasma synthesized particles are collected either as a deposit on a substrate or as powder on the electrostatic precipitator

The yield and characteristics of the synthesized nanomaterials depend strongly on

- (i) The properties of the precursors
- (ii) The geometry of the atomizer
- (iii) The atomizing and spray
- (iv) Process variables

1 4 7.2 Flame pyrolysis

Flame based methods for synthesis of nanoparticles are desirable because the processes are continuous the product is free of contamination. On introduction of the precursor solution into the flame solvent vaporization and particle formation occurred in the reactor. The resulting nanoscale particles were collected downstream of the flame using a movable water cooled nitrogen quenched collection probe.

Helble et al.¹⁴ reported the synthesis of spherical nano particle by dissolving zirconium(IV) *n* butoxide in butanol and subsequently introducing the precursor into the flame through a high pressure atomizer with a size range of 160 nm.

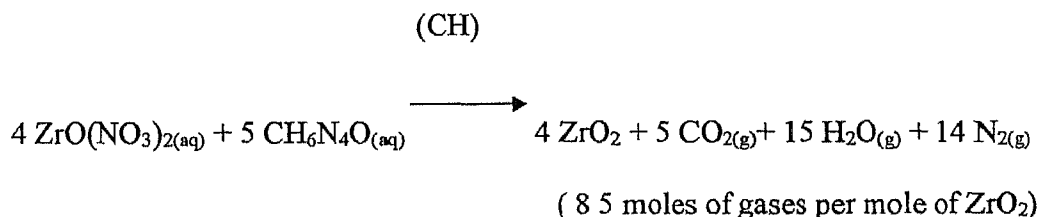
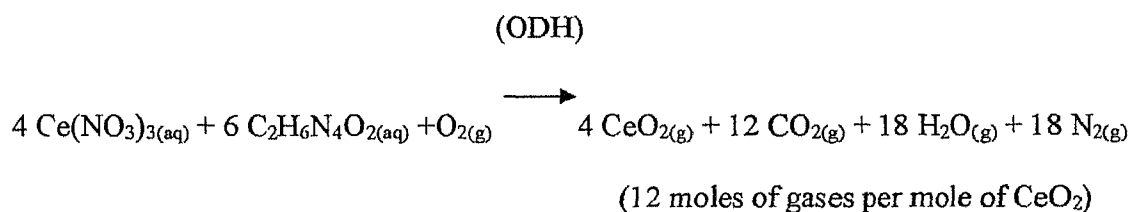
1 4 7 3 Combustion synthesis

Patil and Aruna¹⁵ used Cerous nitrate $\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ and zirconyl nitrate $\text{ZrO}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ as the source of cerium and zirconium to synthesize ceria –zirconia solid solutions with an average crystallite size of 5–11 nm and high surface area in the range of 36–140 m²/gm by the process of combustion. Carbohydrazide/ oxalyl dihydrazide prepared from diethyl carbonate / diethyl oxalate and hydrazine hydrate

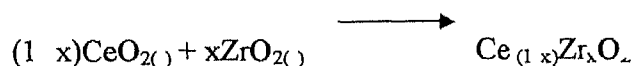
were used as fuels. The preparation of $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ requires a redox mixture containing cerous nitrate, zirconyl nitrate and CH (carbohydrazide) in the molar ratio of 1:1:1.

In a typical combustion reaction, a pyrex dish containing an aqueous redox mixture of stoichiometric amounts of cerous nitrate, zirconyl nitrate and CH is introduced into a muffle furnace preheated to $350 \pm 10^\circ \text{C}$. The solution boils and froths, followed by the appearance of flame, yielding a voluminous product.

Formation of ceria, zirconia and ceria-zirconia solid solutions from the cerous nitrate-ODH and zirconyl nitrate-CH redox mixtures can be written as



Solution combustion of cerous nitrate, zirconyl nitrate and CH/ODH redox mixture in the appropriate ratio gives desired $\text{Ce}_{(1-x)}\text{Zr}_x\text{O}_2$ ($x=0.2$ to 0.9).



The combustion reaction was vigorous/violent when the ceria content is more and the products flew out of the container during combustion. Formation of CeO_2 from the Cerous Nitrate – ODH redox mixture requires atmospheric oxygen for the oxidation of Ce^{+3} to Ce^{+4} during the combustion. The combustion reaction with CH fuel were not

vigorous when the zirconia content is more in the stoichiometry. This could be explained based on the difference in the heats of combustion of zirconyl nitrate-CH and cerous nitrate-CH redox mixtures. From the thermomechanical calculations for the above stoichiometric equations it was found that the heat of combustion of cerous nitrate-CH redox mixture is very high (1906.23 KJ/mol of CeO_2) compared to that of zirconyl nitrate-CH mixture (439.15 KJ/mole of ZrO_2). In order to reduce the exothermicity of the cerous nitrate-CH combustion, a fuel lean redox mixture i.e. 0.94 mol of CH (stoichiometric amount = 1.875 mol) per mol of cerous nitrate was used. The combustion of fuel lean redox mixture was not vigorous.

1.4.8 Sonochemical Method

Sonochemical processing has been proved to be a useful technique in the synthesis of novel materials with unusual properties. Jun Lin et al.¹⁶ has reported for the first time that nano porous ceria and ceria-zirconia solid solutions with high surface area can be obtained directly via high intensity ultrasound irradiation.

A total of 0.02 mol of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and 0.4 mol of urea were dissolved in 100 ml of deionized water. The solutions were sonicated continuously for 3 h (amplitude 80%) by a high intensity ultrasonic probe with diameter 13 mm (20 KHz, 100 W/cm²). During the sonication, the temperature of the solutions was raised to about 80 °C. For the synthesis of $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$, 50 ml of deionized water was added as soon as the gel formed in the solution. The resulting powders were collected by centrifugation, washed thoroughly with deionized water and ethanol and dried in a vacuum oven overnight at 383 K. The composition of the solid solutions was changed by

varying the molar ratio of Ce to Zr in the starting solutions while maintaining the total amount of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ at 0.02 mol

Pang et al.¹⁷ also investigated sonochemical method in preparing stable colloidal hydrous YSZ without the presence of a surfactant by dissolving 0.08 mole of Y_2O_3 and 0.92 mole of $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in nitric acid and deionized water under heating and stirring respectively. Then NH_4OH was added drop wise into the mixed solution under sonication that resulted in formation of as prepared colloidal hydrous YSZ nanoparticles with a particle size of ~ 27 nm (measured by analytical ultracentrifugation AUC). The as prepared YSZ aqueous suspension was not stabilized since it coagulated after short time by the condensation of the surface hydroxyl group. A stable hydrous YSZ suspension with a particle size of ~ 2.8 nm was obtained by redissolving the water-ethanol washed product into absolute ethanol and then sonicating for 30 minutes.

1.4.9 Powder preparation by precipitation

Precipitation of hydrous zirconia from an aqueous solution containing zirconium salt can occur in different ways such as by simply aging the aqueous solution of zirconium salt at lower temperature for several days, adding of a base i.e. either ammonium hydroxide or urea, uniform heating of an alcohol water solution containing salt of zirconium etc.

1.4.9.1 Forced Hydrolysis

This method consists of preparing a solution of $\text{ZrOCl}_2 \cdot x\text{H}_2\text{O}$ in water and aging it at nearly 100°C for several days. In the fresh aqueous solution of ZrOCl_2 a tetramer $[\text{Zr}(\text{OH})_2 \cdot 4\text{H}_2\text{O}]^{+8}_4$ exists with a radius of gyration of 4.5°A . Aging of the solution

even at room temperature for several months leads to formation of species with larger radius of gyration. When aging is carried out at 100⁰ C particles of ZrO₂ form.

Hu *et al*¹⁸ have studied forced hydrolysis method by preparing aqueous solution of zirconyl chloride and incubating it at 100⁰C for 3 days. The authors obtained nearly cube shaped nano sized particles with narrow size distribution (~50 nm average size) by using this technique. In their investigation they found that initially the particle size increased with ZrOCl₂ concentration (M) due to enhancement of hydrolysis kinetics reaction but after a critical concentration of 0.2M, the particle size again decreased due to inhibition of reaction kinetics because of high acidity.

The hydrolysis reaction can be expressed as follows



Later Murase *et al* have reported that the primary and secondary particle sizes of hydrous zirconia synthesized through the hydrolysis of ZrOCl₂ aqueous solutions are controlled by the concentrations of H⁺ and Cl⁻ ions produced during hydrolysis. The authors have found that the average secondary particle size of hydrous zirconia increases as the H⁺ ion concentration increases, reaching a maximum value of 200 nm when H⁺ ion concentration becomes 0.44 mol dm⁻³ and on further increase of H⁺ ion concentration it tends to decrease.

In another work Kato *et al* have reported that the formation rate of hydrous zirconia particles synthesized from ZrOCl₂ solutions containing various metal chlorides is affected by the number of Cl⁻ ions in the aqueous solution. This was also verified by Matsui and Ohgai who reported that the formation rate of hydrous zirconia particles decreased as the

ZrOCl₂ concentration increased or the temperature decreased. This may be attributed to the Cl⁻ ions attracted to the primary particle surface hindering crystal growth.

Matsui et al.¹⁹ have extensively studied the formation mechanism of hydrous zirconia particle by hydrolysis of ZrOCl₂ solutions. They found that the primary particle size of hydrous zirconia particles decreased as the ZrOCl₂ concentration increased and was independent of the reaction temperature. The secondary particle size of hydrous zirconia particles synthesized at ZrOCl₂ concentrations of 0.1, 0.2, and 0.4 mol/dm³ first increased monotonously and then decreased, and also the particle size decreased monotonously as the reaction temperature decreased. They proposed that ZrOCl₂ · 8H₂O dissolves in aqueous solution forming a tetramer complex $[\text{Zr}(\text{OH})_2 \cdot 4\text{H}_2\text{O}]^{+8}_4$ which deprotonates on heating giving rise to a polymeric species $[\text{Zr}(\text{OH})_{2+x} \cdot (4-x)\text{H}_2\text{O}]^{(8-4x)+}$. When the concentration of this polymeric species reaches a critical supersaturation level, crystal nuclei of hydrous zirconia is generated. These nuclei grow in due course to form primary particle of hydrous zirconia. Secondary Particles of hydrous zirconia are formed by hard aggregations among the particles. The author reported that the primary particle size of hydrous zirconia decreases as the concentration of ZrOCl₂ · 8H₂O is increased. The crystal nucleus of the hydrous zirconia produced by the polymerization of $[\text{Zr}(\text{OH})_{2+x} \cdot (4-x)\text{H}_2\text{O}]^{(8-4x)+}$ formed an electric double layer between the H⁺ ion adsorbed onto the surface hydroxyl group and the Cl⁻ ions attracted to the surface on the crystal nucleus. As the concentration of ZrOCl₂ increases, the amount of H⁺ and Cl⁻ ions produced during hydrolysis is also increased, resulting in an enhancement of the thickness of electrical double layer. This electrical double layer interferes with the polymerization of the crystal

nucleus and thus the crystal growth of the primary particles is affected by the amount of ZrOCl

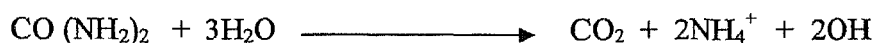
The primary particle size decreases with increase in H^+ ion concentration that causes an increase in surface energy of the primary particles. This eventually causes more aggregation among the primary particles and leads to increase of the secondary particle size with increase in H^+ ion concentration. But after reaching a critical concentration of H^+ ion (0.4 mol dm^{-3}) electric double layer repulsion hinders aggregation among the primary particles and causes decrease in the secondary particle size with further increase in H^+ ion concentration. The decrease in secondary particle size with decrease in temperature reaction temperature is attributed to the increase in the dielectric constants and the decrease in the surface potentials as the reaction temperature decreased.

1.4.9.2 Precipitation by using of a base

Earlier we have discussed that hydrolysis of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ produces H^+ and Cl^- ions. So if pH of the solution is increased the equilibrium will be shifted towards the product side and to maintain the pH level more hydrolysis will occur producing hydrous zirconia. This can be done by addition of strong bases like NH_4OH , NaOH or slowly by addition of urea and subsequently heating the mixture. Hydrolysis by ammonia leads to the instantaneous formation of white precipitate of hydroxide and the hydrolysis reaction is difficult to control. But when urea is used for hydrolysis reaction the pH of the solution increases slowly by a two step hydrolysis of urea producing NH_3 and CO_2 . In this case the process can be controlled more easily.

Huang Yue xiang and Guo Cun ji²⁰ have studied urea hydrolysis method by dissolving $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (with various concentrations) and urea $[\text{CO}(\text{NH}_2)_2]$ into distilled

water and then boiled continuously for 50 hours in a closed system that resulted in the formation of colloidal sol. It is well known that zirconyl ions (Zr^{+4}) are present as $[Zr_4(OH)_8 \cdot 16H_2O]^{8+}$ tetramers in aqueous solution. During urea hydrolysis, when zirconyl chloride octahydrate is dissolved into water, the four coordinated water molecules are replaced by hydroxyl ions obtained from the decomposition of urea according to the following reaction:



Condensation between the hydroxyl ions coordinated groups produce fluffy crystal nuclei which grow with boiling time to form monoclinic phase. During urea hydrolysis, the pH of the solution decreases at the initial stage due to $ZrOCl_2$ hydrolysis, which is followed by urea decomposition that leads to increase in pH of the solution. At longer boiling time period, pH value becomes nearly constant due to equilibrium of these two chemical reactions. The agglomeration of the hydrolysis products was proposed to depend on the pH of the solution, i.e., amount of OH^- present. Higher the pH, faster is the agglomeration.

Srinivasan et al.²¹ also worked on the synthesis of zirconia nano powder by using NaOH as a base and claimed that a pure cubic phase was originated at 500°C starting from a precursor precipitated at pH=13.5.

In another work, Lin Wu and Ton-Fon Wu²² have reported the preparation of Hydrated ZrO_2 powder via a conventional precipitation process. Ammonia was introduced into an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ (0.03M) and YCl_3 (3 mol%) to induce condensation. The precipitate was washed thoroughly with deionized water and then dried at a temperature of 70°C in air. The surface pretreatment was conducted by

placing the hydrous precursor powder in a closed container into which the OH scavenging reagent— namely hexamethyldisilazane ($((\text{Si}(\text{CH}_3)_3)_2\text{NH})$) was injected (5 ml/gm of powder) The entire container was heated at 150°C for 1 h The powders were calcined in air at increasing temperatures from 300 °C up to 1100°C with increments of 100°C a heating rate of 100°C/h and a hold time of 1 h The pure ZrO_2 powder (Not surface treated) exhibited exclusively the *m* ZrO_2 phase for calcination at 400°C For the 3Y ZrO_2 (not surface treated powder) powder on the other hand showed predominantly *t* ZrO_2 within a temperature range (300°– 400°C) However the *t* ZrO_2 content decreased with continued heating at higher temperatures from 87% at 400°C to 18% at 900°C The size of the ZrO_2 crystallites in the powder increased as the calcination temperature increased from 8 nm at 400°C to 25 nm at 900°C However the surface treated powder that was calcined at 1100°C with an average crystallite size of 16 nm exhibited only *t* phase In contrast the transformation to *m*- ZrO_2 occurred in the 3Y- ZrO_2 (untreated powder) merely after calcination at 400°C

This can be explained based on the hypothesis that the metastability is due to a lower surface free energy of *t* ZrO_2 than that of *m* ZrO_2 Accordingly *t* ZrO_2 nanocrystallites occur spontaneously as long as they are small enough to produce a sufficiently large (specific) surface to compensate the difference in bulk energy Accordingly the enhanced stability as observed in the surface treated powders can be attributed in part to their suppressed grain growth rate which is effected by the HMDS treatment

1 4 9.3 Homogeneous precipitation by heating alcohol water solution

All the precipitation processes discussed are associated with some drawbacks mainly that they yield an agglomerated product with wide size distribution Furthermore many of them are very slow

When a ZrOCl_2 solution with an alcohol water mixture as a solvent is heated the dielectric constant of the solution decreases significantly As a result the salt solution becomes supersaturated and precipitation occurs The phenomenon has been used to prepare spherical ZrO_2 nanoparticles Guo et al²⁵ investigated the preparation of zirconia nano particle by this method They dissolved 97 mol% Zirconyl Chloride octahydrate and 3 mol% yttrium nitrate in dilute alcohol –water mixture PEG was added as a dispersant The starting solution was uniformly heated to 75°C in a thermostat bath and kept at this temperature for certain time when solution turned into white gel pH was adjusted to 9 by the addition of NH_4OH and washed repeatedly with distilled water for complete removal of Cl^- ion dewatered by ethyl alcohol dried at 120°C for 12 hrs and calcined at 600°C for 2 hrs The powder was isostatically pressed at 400 MPa and sintered at 1150°C for 2 hrs They have found an increase in specific surface area of the powder from $53\text{ m}^2/\text{gm}$ to $65\text{ m}^2/\text{gm}$ by using PEG as a dispersant This can be explained by the steric stabilizing effect of PEG preventing agglomeration of particles As both zeta potential and dielectric constant affect the electrostatic repulsive force between the particles the kind of solvent mixture plays a crucial role in the precipitation and morphology of the resulting particles They have also studied the effect of volume ratio of ethanol and water on the powder size and reaction rate and found that when R/H ratio is too low the reaction is much slower and when the R/H ratio exceeds some critical

value the powders have no obvious difference. The optimum R/H ratio was reported to be 5:1. The author reported a powder green density of 47% after cold pressing and a sintered density of 98% with an average grain size of 98 nm.

Microwave heating of alcohol/water/salt solution has some distinct advantages over the conventional heating technique in respect of particle size and morphology. Particles formed under conventional heating method were polydisperse, agglomerated, spherical or irregularly shaped because of inhomogeneous precipitation through the temperature gradient, the shear force induced by stirring, compositional non-uniformity and the low heating rate. Microwave heating provides (a) uniform volumetric heating and (b) rapid heating rate preventing agglomeration and higher polydispersity of the precipitated powder. Moon et al.²⁴ investigated a novel method that yielded spherical ZrO_2 precursor powders of narrow size distribution through microwave heating of zirconyl chloride solution with an alcohol/water mixture as the solvent. They studied the variation of dielectric constant and precipitation temperature with volume ratio of 2-propanol to water (R/H). The authors found that particle size and particle agglomeration level could be controlled by amount of the surfactant (hydroxypropyl cellulose, HPC) in the solution and reported a mean particle size of $0.2 \mu\text{m}$ at HPC concentration of $3 \times 10^{-3} \text{ gm/cc}$, R/H 5, salt concentration 0.2 M .

Jean and Ring²⁵ studied the effect of sterically stabilizing surfactants during synthesis of unagglomerated monosized ceramic powders in order to give dense and uniform green compacts. TiO_2 powder was synthesized by hydrolysis of titanium ethoxide in alcohol solution in presence of HPC. The authors proposed two unique properties that any sterically stabilizing dispersants must have. Firstly, the dispersant

must allow polymeric reaction products to diffuse through the adsorbed layer. Secondly, the dispersant must not be incorporated into the structure of the growing particles, i.e. it must be physically adsorbed and not chemically binding to the surface. They also showed that reaction yield decreased from 68.1% to 58.3% and particle number density increased from 5.5×10^{10} to 9.2×10^{10} per cc when HPC concentration was increased from zero to 1.71×10^{-3} gm/cc. The HPC molecules do not act as heterogeneous nucleation sites and prevent agglomeration during growth even when higher reactant concentration is used.

Jindal²⁶ have prepared monodispersed nanoparticles of hydrous ZrO_2 , $\text{ZrO}_2 \cdot \text{Y}_2\text{O}_3$ and $\text{ZrO}_2 \cdot \text{Gd}_2\text{O}_3$ by using the same method as Moon et al.²⁶ The author has studied the influence of various factors such as concentration of the salt, rate of heating and heating time on size and morphology of the particles and found that for 0.1M, 0.05M and 0.01M ZrOCl_2 concentration, nearly spherical monodispersed particles of sizes 305 nm, 200 nm and 144 nm respectively are produced when no dispersant is used. The particle size decreases by a factor of 4 (i.e. from 430 nm to 100 nm) when the heating time is decreased from 60 s to 10 s. Effect of dispersants was also investigated by adding small amounts of sodium hexametaphosphate (SHMP), acetylacetone (AcAc). Addition of AcAc decreased the particle size significantly from 350 nm to 150 nm when 1 ml AcAc was added to a 0.1M ZrOCl_2 solution. Higher concentration of AcAc completely suppressed the precipitation of particles.

In a recent study Paul²⁷ has reported the particle size of 35 nm can be prepared from a $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$ solution of 0.05 M at HPC concentration of 1.71×10^{-3} . The author has studied the particle size and morphology of hydrous zirconia particle in mother liquor by Transmission Electron Microscopy. In his work Paul²⁹ investigated the effect of zirconyl

chloride concentration on particle size of zirconia keeping the surfactant concentration fixed at 1.71×10^{-3} gm/cc and found that particle size increases almost linearly from 35 nm to 200 nm with increase in $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$ concentration from 0.005 M to 0.1 M

1.5 Statement of the problem

As discussed above homogeneous precipitation method is very attractive for preparation of nanosized zirconia particles with narrow size distribution. Use of an organic solvent in aqueous solution containing metal salt reduces the dielectric constant of the mixture and when the solution is heated it becomes supersaturated and precipitation takes place since the solubility of the salt decreases with increase in the temperature.

In an earlier study preparation of nano suspension of ZrO_2 by heating alcohol water solution containing zirconyl chloride was reported. Present study is a reinforcement of some that work carried out earlier. It is very difficult to flocculate these zirconia nano particles in the suspension because the steric stabilizing effect offered by surfactant dominates over electrostatic force of attraction and repulsion. Separation of the suspended nano particle in the form of dried nanozirconia powder is proposed to be investigated. Preparation of Gd_2O_3 doped zirconia nano powders by the same technique is also proposed to be studied to stabilize the high temperature phase of ZrO_2 from room temperature to sintering temperature. This is useful in application requiring sintered bodies where if not stabilized the zirconia ceramics fail under the phase transformation strains during cooling after sintering.

One step microwave treatment produces a nano zirconia suspension with somewhat wider size distribution as reported in the earlier work. Monodisperse ceramic

particles or particles with very narrow size distribution are of great importance because these particles can give better packing density and thereby a significant improvement in green and sintered densities besides having other applications. An effort to produce nano particles of zirconia with narrower size distribution is also planned to be undertaken.

Nanoparticles have a high surface to volume ratio so that their properties are dominated by the surface characteristics. The surface properties of nano particle can be modified by coating it with a second phase. To modify the surface of zirconia nanoparticles by sol gel technique is proposed to be investigated.

Use of particles to reinforce various materials is well known. Introduction of particles of a second phase can significantly alter the various properties of a matrix phase. In situ precipitation of nanoparticles of metals in glass phase prepared by sol gel method has also been reported. However use of mixing methods to prepare composite sol gel films has been studied on a limited scale. The major problem is to obtain a uniform dispersion of the particles of the film. In the present work we propose to study this problem in the case of zirconia particles in a sol gel silica film.

CHAPTER 2

EXPERIMENTAL

2.1 Preparation of Zirconia Powder

2.1.1 Standard method for preparation of zirconia powders

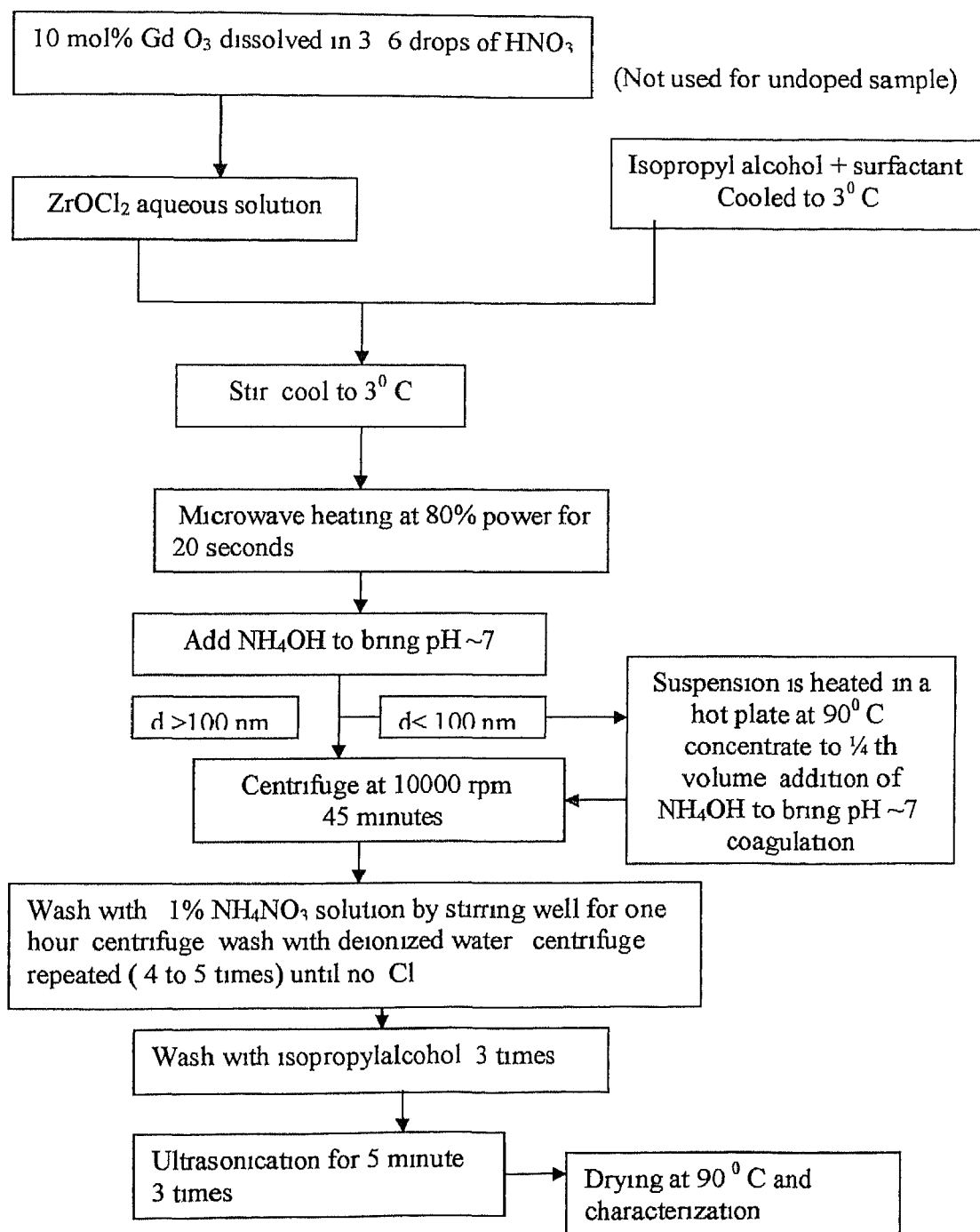
The starting materials used for preparation of zirconia powders are given in Table 2.1 below. All reagents and solvents were used in the as received form with no further purification.

Table 2.1 Starting materials for synthesis of zirconia powder in the laboratory

Materials	Molecular weight	Source	Assay
Zirconyl Chloride Octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$)	322.25	C. S. Zircon Products India	99.5%
Isopropyl Alcohol ($\text{C}_3\text{H}_7\text{OH}$)	60.10	NICE India	99%
Hydroxypropyl cellulose (HPC)	80,000	Aldrich Chemical Company Inc. USA	
Gadolinium Oxide (Gd_2O_3)	362.50	Kemphasol India	99.9%
Ammonia Solution (25% NH_3)	17.024	NICE India	99.9%
Ammonium nitrate	80.45	NICE India	99.9%

The flowchart of the processes used for the preparation of undoped and 10 mol% Gd_2O_3 doped hydrous zirconia suspensions are described below.

2.1.2 Preparation of undoped and 10 mol% Gd_2O_3 doped zirconia powder



An ordinary kitchen microwave (2450MHz 1350W \pm 10% BPL India) was used for the purpose of heating the precursor solution. The microwave could operate at 0-100% of full power. A refrigerator (LEONARD Model No. 126A106174 Capacity 165 liter) was used for cooling of the solution.

The concentration of zirconyl chloride was varied from 0.01M to 0.05M and the volume ratio of iso-propyl alcohol to water in the starting solution was 5. The dispersant used was hydroxypropyl cellulose (HPC). The concentration of HPC was also varied from 0.5×10^{-3} gm/cc to 1.71×10^{-3} gm/cc to study the effect of dispersant on particle size and morphology. The volume of the salt solution was either 5 ml or 10 ml and the corresponding isopropanol volume was 25 ml or 50 ml. The amounts of the various ingredients actually taken are given in table 2.2.

Table 2.2 Quantities of different ingredients taken for preparation of Zirconia powder

ZrOCl ₂ 8H ₂ O Conc (M)	Calc weight of ZrOCl ₂ 8H ₂ O (gm)	Actual weight of ZrOCl ₂ 8H ₂ O taken (gm)	Water (ml)	Isopropan ol (ml)	Conc of HPC gm/cc	Calc Weight of HPC (gm)	Actual weight of HPC taken (gm)
0.01	0.1933	0.1947	10	50	1.71×10^{-3}	0.1026	0.1030
0.02	0.3867	0.3867	10	50	1.71×10^{-3}	0.1026	0.1040
0.03	0.579	0.5795	10	50	1.71×10^{-3}	0.1026	0.1031
0.04	0.773	0.775	10	50	1.71×10^{-3}	0.1026	0.1030
0.05	0.966	0.9654	10	50	1.71×10^{-3}	0.1026	0.1018

Required volume of isopropyl alcohol was taken and required amount of dispersant (HPC) was added to it and stirred well for 45 minutes so that HPC was fully dissolved in the solvent. This solution was cooled to 3°C in the refrigerator. Zirconyl chloride aqueous solution was added to this pre-cooled isopropyl alcohol and stirred well. For preparation of Gd_2O_3 doped sample, the required amount of Gd_2O_3 was dissolved in 3–6 drops of concentrated HNO_3 and the solution was added to the aqueous solution of zirconyl chloride prior to the addition of HPC solution to this. This starting solution was again cooled at 3°C . The solution was then taken out quickly from the refrigerator and was heated in the microwave oven for 20 seconds at 80% power.

When the starting solution was heated, it became supersaturated and precipitated shortly since solubility of the salt decreases with increase in the temperature. To avoid shear-induced agglomeration, the starting solution was uniformly heated in the microwave chamber without stirring. Just after taking out the solution from the microwave, the pH was ~ 1.24 .

2.3 Nucleation and Growth Study

For studying nucleation and growth, the precursor solution was nucleated at 80% and 100% microwave powers for 5, 10 and 15 seconds respectively and then aged at 50°C for 0 to 9 hours of time. The particle size of the suspension was measured just after the nucleation and after different time intervals of aging at 50°C by HPPS. Experiments were also done by filtering the precursor solution through 0.2 micron filter paper to avoid the discrepancy in particle size value due to dust particles and cooling the syringe filter to 3°C by passing the cold alcoholic solution through it. Aging of the zirconia suspension

was done inside the HPPS instrument by setting the temperature of the equipment at 50⁰ C

2.4 Separation of Hydrous Zirconia particles from the mother liquor

Hydrous zirconia particles prepared from precursor concentration of 0.01 M and 0.02 M are very stable in suspension and can not be separated merely by centrifugation. The following method was followed to settle the hydrous zirconia particle so that it can be washed and dried subsequently.

A 200 ml of such suspension was heated in a hot plate kept at 80⁰ C and the suspension was evaporated and thus concentrated to 50 ml. After cooling the suspension to room temperature, dilute NH₃ solution was added to bring the pH to ~7.8. The particles were coagulated and could easily be washed by centrifugation.

2.5 Washing and drying of as prepared hydrous zirconia powder

The precipitates were washed with lukewarm 1% NH₄NO₃ solution by stirring for approximately 1 hour and then centrifuged at ~10000 rpm for 30 minutes and then washed with water by stirring for 30 minutes followed by centrifugation. The process was repeated for 3 – 4 times until complete removal of Cl⁻ ion from the precipitates as confirmed by the addition of AgNO₃ to the drained supernatant liquid after every centrifugation.

The water washed precipitates were then washed with propanol at least for three times by stirring for ~2 hours and again centrifuging at ~10000 rpm for 30 minutes to remove propanol. The propanol washed precipitate was divided into four parts and each part was suspended in 100 ml fresh propanol to make a dilute suspension. To suspend the alcohol washed precipitate in fresh propanol it was ultrasonicated for 10

seconds three times. The washed and resuspended sample was then dried at 90°C in an oven for around 1.5–2 hours.

2.6 Crystallization of washed, dried powder of hydrous zirconia

The hydrous zirconia powder synthesized by microwave was amorphous in nature. So it was made into crystalline form by calcination technique.

For calcination the required amount of powder was taken in a ceramic boat and heated at 200°C, 400°C and 600°C and 900°C respectively for one hour. The undoped zirconia powder was calcined at 200°C, 400°C and 600°C respectively for one hour. The 10 mol% Gd₂O₃ doped zirconia powder was calcined only at 600°C and 900°C for the same period of time.

2.7 Characterization of Powders

The powders were characterized using High Performance Particle Size analyzer (HPPS), Transmission Electron Microscope (TEM), Scanning Electron Microscope, X-Ray Diffraction (XRD), BET surface area analyzer. Different instruments that were used for characterization are listed below.

Table 2.3 Instruments used for characterization

Characterization Tool	Model	Company
High Performance Particle Size Analyzer		MALVERN INSRUMENTS United Kingdom
Transmission Electron Microscope	FX 2000	JEOL Japan
Scanning Electron Microscope	JSM 840 A	JEOL Japan
X Ray Diffraction	ISODEBYEFLEX 2002	RICH SEIFERT & CO Germany
BET Surface Area Analyzer	VECTOR 22	COULTER

2 7 1 Measurement of Particle Size by High Performance Particle Size Analyzer

There are two options for measuring particle size value by High Performance Particle Size Analyzer namely manual mode and SOP (Standard Operating procedure) mode. In the present study manual measurement was performed by selecting Measure Manual. The measurement parameters dialogue (with three tabs) appeared and allowed the operator to set all measurement options. These three tabs are *documentation*, *sample setup* and *measurement setup* tab respectively. The *documentation* tab gives the option of sample name and also comments on the sample. Temperature solvent or dispersant properties (viscosity and refractive index) and sample property (refractive index for calculation of volume distribution) are fed in the *sample setup* tab.

Measurement setup tab allows a control over accuracy and repeatability of the measurement quality by Normal Enhanced and Custom settings. The difference between normal and enhanced setting is the time it takes to make a measurement. An enhanced quality measurement may take much longer time compared to normal quality measurement and will give more stable distributions. The custom setting can be used to manually define the number of runs and run duration. In the present study, it has been found that the HPPS run in the custom setting produced inconsistent results.

The fundamental size distribution generated by DLS technique is an intensity distribution. The X axis shows a distribution of size classes while Y axis shows relative intensity of the scattered light. The results section gives three information i.e. Z average size (also known as cumulants mean), polydispersity index and peak modes.

2.7.2 Sample preparation for particle size measurement of particles in mother liquor by HPPS

Measurement of particle size by HPPS requires a well dispersed stable suspension which does not settle during the entire measurement. Hydrous zirconia suspension prepared from a precursor concentration of upto 0.03 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ is stable enough for measurement within a time range of 4 hours. But samples prepared from a precursor concentration greater than 0.03 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ settle down fast (just after few minutes of preparation). So these need further treatment for HPPS measurement.

For this, first 1.0×10^{-3} gm/cc of HPC was dissolved into propanol. Then few drops of the mother liquor (usually 35 drops) are added to this propanol HPC solution (usually 15 ml). This suspension was stirred well and subjected to

ultrasonication for better dispersion. After that the sample was measured for particle size by HPPS.

2.7.3 Sample preparation for particle size measurement of dried powder by HPPS

Dried powders also need further treatment for better dispersion. For this purpose, 0.01 gm of powder was added to 30 ml of propanol containing 1.0×10^{-3} gm/cc of HPC. Then the solution was stirred well and ultrasonicated to break the agglomerates. Then few drops of this suspension (usually 35 drops) were again added to 15 ml of propanol HPC solution and again stirred and ultrasonicated for better dispersion. After that the sample was ready for measurement by HPPS.

2.8 Measurement of Viscosity

Viscosity values of the solvent/dispersant are required by HPPS for measuring the particle size of any suspension.

Viscosity of the suspensions was measured by using THE BROOKFIELD DIGITAL VISCOMETER (LV model). The operating procedure and precautions during measurement are given in appendix B. Table 2.1.4 shows a typical example for measurement of viscosity for a sample.

Table 2.4 Measurement of viscosity for zirconyl chloride suspension

Spindle number	Speed (rpm)	Sample details	Factor	Actual reading	Viscosity (cps)
18	12	0.01M ZrOCl_2	2.0	3.2	6.4
	30	$8\text{H}_2\text{O} \cdot 1.71 \times 10^{-3}$	1.0	6.1	6.1
	60	gm/cc HPC pH=2.41	0.5	11.0	5.5

To convert viscometer dial reading to viscosity (in centipoises or mPa s) the actual dial reading should be multiplied by the corresponding factor for corresponding speed. From the above Table it is observed that for 60 rpm speed viscometer dial reading is 11.0. So this reading must be multiplied by the corresponding factor i.e. by 0.5 and ultimately viscosity becomes 5.5 centipoise.

2.9 Preparation of samples for TEM observation

2.9.1 Preparation of Formvar solution for coating of TEM grid

A 2% solution was made by dissolving 2 gm of formvar powder (Ernest F. Fullam Inc. NY) in 100 ml of chloroform and shaken slightly and then kept overnight so that the formvar dissolved fully. Then the solution was filtered through Whatman 41 filter paper to remove impurity materials. Initially 0.4, 0.5 and 1% solution were prepared but these produced so thin film that it was not possible to separate from the glass slide. Therefore 2% solution was considered to be the optimum concentration for producing the thin film. The film thickness also depends on other factors like speed with

which formvar solution is taken out of the funnel. If the speed of the formvar is high then it gives thick film and if slow then it gives a thin film.

2.9.2 Procedure for coating of TEM grids

For coating of TEM grids following items were required

- 1 Copper grids Type G400 (Polaron Equipment Ltd, Watford, England) with mesh size 300 (i.e. 300 parts per inch) and diameter 3.05 mm
- 2 Poly vinyl formal formvar (Ernest F. Fullam Inc., NY)
- 3 Scalpel Blade with handle
- 4 Fine pointed forceps (VIGOR, B. Jadow Inc., Switzerland)
- 5 Separating funnel with a stop cock (50 ml)
- 6 Distilled water
- 7 Glass slides (Blue Star)
- 8 Petridish

First glass slides were washed with vim powder and then with distilled water before rinsing it with acetone. The slides were gently wiped by a tissue paper. To further check if the slides were clean, the slides were seen against light and if there were any spots, then those were removed because the film sticks there and then it becomes extremely difficult to take out film from slide.

Formvar solution was poured in 25 ml funnel after closing the cock in such a way so that almost half of glass slide could be immersed within formvar solution. Now the glass slide was put within formvar solution gently and the stopcock was opened. The speed of the draining solution can be changed according to the thickness required but one constant speed should be maintained throughout. The slide was gradually taken

out of the funnel after draining out of the whole solution. Normally there was some liquid remaining at the end of the slide. Now a formvar film adhered at both sides of the slide. If the film is too thick then it shows coloration. But if it is thin then it is difficult to make out as to how much area it is covering. This can be checked by blowing some air from mouth that makes the film visible.

With the help of a blade the corners of film were scraped off and then that end of the slide is immersed in water. Then with the help of a knife one end of the film is separated from the slide. Once one end of the film starts coming out, the rest comes slowly due to force exerted by water. Sometimes it is difficult to separate the last end of the film from the slide. So at that time it is wise to cut that end with great care so that the other part of the film is not damaged. Once all of the films comes out it floats on water. With the help of a forecep grid was then was put on the film so that dull or rough side adhered to film (that is upside down). Another glass slide was taken and its' one end was gently put on one end of the film and quickly raised so that film also came on the slide along with the grid positioned in between film and slide. The coated grid was dried under a lamp for 30 minutes.

2.9.3 Sample preparation for mother liquor and dried powder for TEM analysis

The sample preparation technique for mother liquor and dried powder has already been discussed in the earlier section. For TEM analysis of the mother liquor small volume of the sample was taken out in a pipette. Then one drop of this suspension was placed over the coated grid still sticking to the glass slide. Care was taken so that the tip of the pipette does not touch the grid, otherwise the fragile coating could break. . The grid was put under a lamp for nearly 30 minutes so that it dried. The grid was then separated

from the glass slide gently using scalpel blade. This grid was then ready for observation in TEM.

For TEM analysis of the dried powder, nearly 0.01 gm of the dried powder was dispersed in 30 ml of solvent (either isopropyl alcohol or water) by ultrasonication with FISHER sonic dismembrator model 300 for 10 minutes. Then the suspension was allowed to cool down to room temperature. The rest of the methods is same as discussed above. The particle size and morphology were observed by using a Transmission Electron Microscope (JEOL FX 2000, Japan). The electron microscope was operated at 120 KV.

2.10 Scanning Electron Microscope

The distribution and morphology of zirconia particles in composite films was observed using a JEOL JSM 840 scanning electron microscope. All micrographs were taken in secondary mode.

The sample for SEM characterization was prepared by depositing a drop of the powder suspension on a glass slide. The dried sample on the glass slide was then coated with Au-Pd, which gives high electrical conductivity to the sample.

A POLARON Sputtering system was used to deposit the Au-Pd thin film in argon environment. The conditions were:

Vacuum = 100 millitorr

Plasma discharge current = 10–12 mA

Plate DC Voltage = 4–5 mV

Time = 25 minutes

This gives a gray black film over the powder. The substrate was then glued to the SEM sample holder to fix it tightly. Carbon paint was used to make contacts between the Au/Pd film and the sample holder to prevent discharging of the secondary electrons.

2.11 Measurement of Zeta Potential

The zeta potential can be calculated if the mobility of the particles under an externally applied electric field can be measured. This electrophoretic mobility is given by

$$\mu = v/E$$

where v is the velocity of the particle under a field $E = V/d$, d being the distance between the electrodes. The zeta potential in SI unit is given by

$$\xi = \frac{3\eta\mu}{2\epsilon\epsilon_0}$$

A 100 ml 0.01 M ZrO_2 suspension in isopropanol was prepared by ultrasonication for 10 minutes. Then the solution was divided into five parts and the pH was adjusted to 3, 4, 5, 6 and 7 by using HNO_3 or NH_4OH . The cell of the electrophoresis apparatus was cleaned by distilled water. Enough of the prepared suspension was poured in the cell so that the platinum electrodes can be half immersed. The electrodes were inserted in the correct position. The microscope was focused to see the particles in the suspension. First the microscope was set to the first wall position of the cell and then it was adjusted at a position 0.136 mm away from the first wall position to focus on the particle in the suspension. Table 2.1 shows a typical example for adjustment of wall position to focus the particles in suspension through the microscope.

Table 2 5 Determination of focal distance of microscope

Initial Wall position (mm)	Going inward (mm)	Focusing position (mm)
12 98	0 136	12 844

A varying voltage from 24 to 80 Volt was applied to the suspensions with different pH. The time taken by the particle for traveling 3 grids in the eyepiece was measured. The polarity of the field was reversed and the measurement was repeated either on same or different particle. At least 5 such pairs of measurements were taken on different particles. The average time taken by the particles for traveling 3 grids was calculated and using the given value of spacing between the grids (0.0467 mm) the average velocity was also calculated. The mobility of particles was derived by taking the distance between the electrodes as 8.79 cm.

2.12 Measurement of silica gel coating on zirconia particle

The silica gel was prepared by mixing together ethyl alcohol, TEOS, water and HCl. The composition of the mixture was 1 ml TEOS, 1 ml water, 0.1 to 30 μL of HCl (to maintain the pH of the suspension 3.5) and the remainder being ethyl alcohol in a total volume of 100 ml. The mixture was stirred for 1 hr. A suspension of zirconia particles of 115 nm (average dia) was then added to bring the concentration of zirconia in the solution to approximately 11×10^{-6} gm/(ml of solution). This suspension was then placed in the cell of the instruments and the measurements were carried out after different times. The zeta potential of the zirconia particles was measured at $27 \pm 1^\circ\text{C}$ because at higher temperature the high vapor pressure of alcohol makes the measurements difficult.

2.13 Studying particle distribution and arrangement in a composite film using TEOS and surfactant (HPC) simultaneously

2.13.1 Preparation of TEOS sol To prepare TEOS sol, 1 ml of TEOS was added to 95 ml of ethyl alcohol, and to this 1 ml of water was added inside the glove box and stirred for 20 minutes. pH of the solution was adjusted from 3.5 to 5 by HCl diluted with ethylene glycol. After adjustment of pH, the total volume of the solution was made 100 ml by adding requisite amount of ethyl alcohol. This TEOS sol was aged in beakers for different days at ambient temperature.

2.13.2 Preparation of TOSOH zirconia suspension TOSOH zirconia suspension was prepared by dispersing 0.005 volume % of powder in isopropanol. HPC solution: First HPC solution in isopropanol was prepared by dissolving required amount of HPC in 30 ml of isopropanol by stirring for 45 minutes. HPC concentrations were varied from 0.002×10^{-3} gm/cc to 0.032×10^{-3} gm/cc of solvent. To this HPC solution, the required quantity of TOSOH zirconia was added and dispersed by ultrasonication for 10 minutes. Zirconia suspension with no HPC was also prepared by the same method.

2.13.3 Preparation of alumina suspension First 0.005 volume % of powder was weighed in a beaker and then 1 ml of water and 29 ml of isopropyl alcohol were added to it and stirred for 10 minutes. The pH of the suspension was adjusted to 4 by using dilute HCl. After adjusting the pH, the suspension was dispersed by ultrasonication for 10 minutes.

30 ml of TEOS sol aged for different days ($\frac{1}{2}$, 1, 2 days) was added to this freshly prepared zirconia or alumina or silica suspension and kept for different hours undisturbed. After different hours of reaction time, the suspension was stirred with a glass

rod and a drop of this suspension was taken on a glass slide. The drop was dried at oven at 60°C / 110°C for 6 hours and observed under SEM.

2.14 X Ray Diffraction

The phases present and the crystallite size were determined by x ray diffraction technique. XRD pattern of the powder sample was taken with a RICH SCIFERT ISO DEBYEFLEX2002 diffractometer using $\text{CuK}\alpha$ ($\lambda=1.54184\text{\AA}$) radiation with a monochromator. The powders of the requisite sample were packed on a glass slide to make the specimens and the surface of the powder was smoothened by pressing another glass slide over it. The powder was soaked with a few drops of methanol for securing adhesion to the glass slide.

The x ray diffraction plot of the samples was taken between $2\theta = 20^{\circ}$ and $2\theta = 80^{\circ}$. The conditions of the diffraction are as follows:

Current voltage	20 mA, 30 KV
Time constant	10 seconds
Beam slit width	2 mm
Detector slit width	0.3 mm
Scanning speed	$3^{\circ}/\text{min}$ in 2θ
Full scale intensity	5 000 or 10 000 cpm

A computer recorded all intensity versus angle data via an interface and produced a plot. The position of peak, corresponding relative intensities and the interplanar spacing (d) were obtained from the computer. The d values were calculated by using Bragg's formula:

$$n\lambda = 2d \sin\theta$$

where n = order of reflection (1) λ = wavelength of incident x ray (1.54184 Å),
 d = interplanar spacing and θ = angle of diffraction

The phase analysis and indexing of the peaks were done by matching the peak positions and relative intensities with standard data (JCPDS files)

The average crystallite size of the powder was found by using Scherrer formula

$$t = \frac{0.9\lambda}{\beta \cos \theta}$$

Where t = crystallite size

λ = wavelength of radiation

β = corrected full width at half maximum (FWHM)

θ = diffraction angle

The intensity – angle data for each plot was retrieved from the computer replotted and analyzed using graphical software

The uncorrected FWHM (B_0) measured from the plot has several components other than broadening due to crystallite size. They are

- (i) Instrumental broadening
- (ii) Broadening due to spectral width i.e. the X ray itself consists of two components having slightly different wavelengths
- (iii) Broadening due to stress in the crystal

Broadening due to the spectral width was corrected by finding the K_{α} doublet separation d at the 2θ value of interest from figure 2.1. Knowing d and B_0 , the uncorrected FWHM for the sample, the value of B , the half width corrected for K_{α} broadening was determined from figure 2.4. For correction of instrumental broadening

the X ray diffractogram of the strain free coarse silicon powder under similar conditions was used. The half widths for the peaks for (111) (220) and (311) corrected for spectral width was obtained as for the sample. This is called b . It is plotted against 2θ (figure 2.3) and the value of b at 2θ corresponding to the sample peak is read from the plot. Now we have B and b the corrected widths of the sample and silicon respectively. Then figure 2.4 is used to read off the values of β/B corresponding to the value of b/B obtained as above. β is the desired half width after correction for structural width and instrumental broadening. This β is used in the Scherrer's formula to determine the crystallite size. For calculation of the crystallite size generally the first peak is considered but for undoped sample the peak at 60° was taken into consideration.

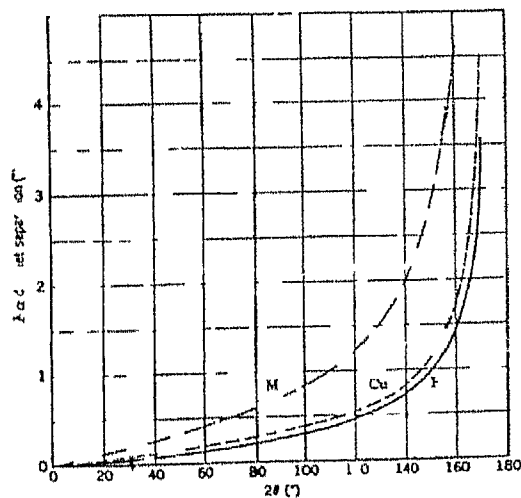


Figure 2.1 Angular separation of the K_α doublet as function of 2θ

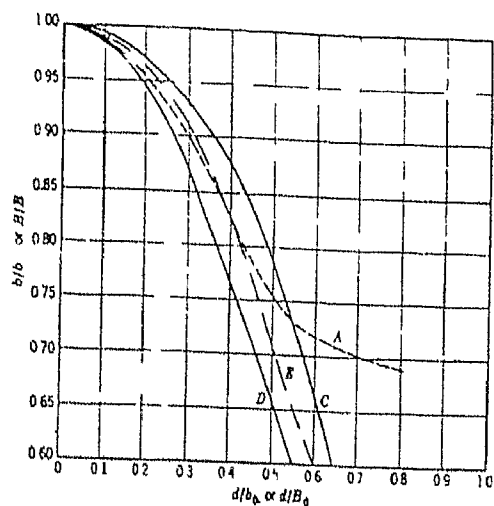


Figure 2.2 Curves for correcting line breadths for the K_{α} doublet broadening

A is for Jones correction curve

C and D are for Gaussian and Cauchy Distribution

B is for profiles intermediate between Cauchy and Gaussian type profiles

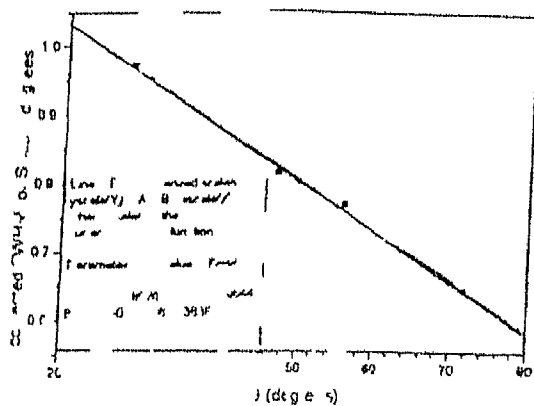


Figure 2.3 Correction full width at half maximum for silicon as a function of diffraction angle

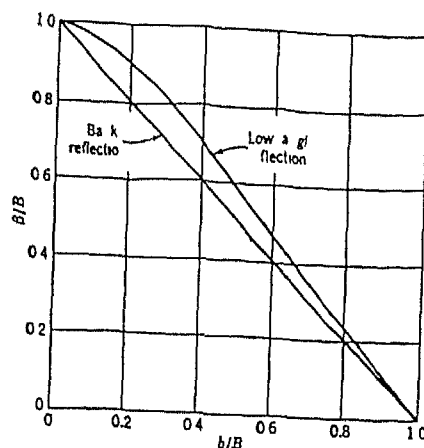


Figure 2.4 Curves for correcting X ray diffractometer line breadths for instrumental broadening under conditions of high resolution

2.15 BET surface area measurement

Minimum of 0.1 gm of powder is required for surface area measurement. The sample was degassed at 120°C for half an hour and then again weighed to determine the losses. The tube containing the sample was then evacuated and dry nitrogen gas was passed through it and the adsorption isotherm was observed. The sample tube is brought back to the room temperature and the desorption isotherm was observed. The surface area was then calculated from the adsorption and desorption isotherm using BET equation.

The particle size was also calculated using the specific surface area data, by the equation

$$\phi = \frac{6}{S\rho}$$

Where ϕ is the average diameter of a spherical particle, S is the surface area of a powder and ρ is the density value of sample.

In calculating the particle size from BET surface area the density of the dried powder was taken as 50 % of the theoretical density (6.1 gm/cc) of zirconia.

CHAPTER 3

Results and Discussion

3.1 Preparation of hydrous zirconia particles by Microwave Heating

Hydrous zirconia suspension was prepared from aqueous ZrOCl_2 solution by adjusting the dielectric constant using isopropyl alcohol and hydroxy propyl cellulose (HPC) as a surfactant to prevent agglomeration. Precipitation occurred on heating from 30°C to $\sim 80^\circ\text{C}$ by microwave heating as discussed in the last chapter. The effects of various variables on particle size and morphology are first described below.

3.2 Effects of various parameters on particle size of hydrous zirconia

3.2.1 Effect of hydroxy propyl cellulose (HPC) concentration

To determine the effect of HPC concentration on the particle size, experiments were conducted using solutions of different HPC concentration but a fixed ZrOCl_2 concentration. The microwave power and duration of heating were kept constant at 80% and 20 seconds. The particle sizes obtained for different HPC concentrations are given in Table 3.1 and plotted in Figure 3.1. The particle size is seen to decrease from 173 nm to 82 nm as the HPC concentration is increased from $0.5 \times 10^{-3} \text{ gm/cc}$ to $1.71 \times 10^{-3} \text{ gm/cc}$ at a fixed ZrOCl_2 concentration of 0.01 M. HPC molecules sterically hinder the process of agglomeration between the particles during precipitations and thus help in minimizing the particle size. At lower concentration, the amount of HPC molecule may not be sufficient for monolayer adsorption onto the particle surface and thus is somewhat ineffective in preventing the particle agglomeration. After a certain HPC concentration (1.71×10^{-3}

gm/cc) there is no benefit of using more HPC because at that concentration the HPC molecule is sufficient to cause monolayer adsorption onto the particle surface and more amount of HPC is of no use to prevent particle agglomeration

Table3 1 Variation of particle size with HPC concentration at a fixed $ZrOCl_2$ concentration of 0.01 M

HPC concentration $g/m \times 10^{-3}/cc$	Diameter (nm)	Width (nm)	PDI
0.5	173.1	17	0.127
0.75	146.6	26	0.152
1	95	27	0.085
1.25	86	22	0.086
1.5	84	21	0.087
1.71	82	20	0.079

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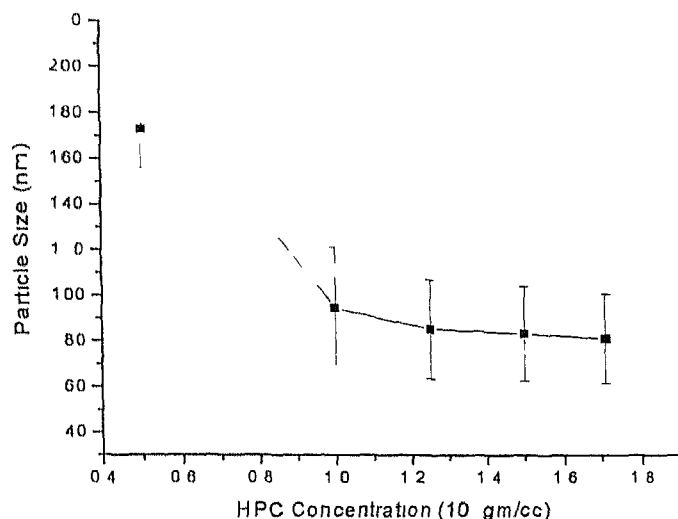


Figure 3.1 Particle Size variation of hydrous zirconia in mother liquor as a function of HPC concentration at a fixed $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration (0.01 M)

3.2.2 Effect of ZrOCl_2 concentration

Effect of ZrOCl_2 concentration on particle size was studied using 0.01, 0.02, 0.03, 0.04, 0.05 M of zirconyl chloride concentration at a fixed HPC concentration (1.71×10^{-3} gm/cc). The results are given in Table 3.2 and plotted in figure 3.2. The experiments showed that the particle size of the hydrous zirconia increases nearly linearly with the salt concentration. This may be explained by the fact as the salt concentration is increased the HPC concentration may not be sufficient to cover up all the nuclei and sterically hinder the particle growth process. Thus a larger particle size is obtained when the precursor concentration (ZrOCl_2) is higher.

Table 3.2 Variation of particle size with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration at HPC concentration of $1.71 \times 10^{-3} \text{ gm/cc}$

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ Concentration (M)	Diameter (nm)	Width (nm)	PDI
0.01	83	35	0.0134
0.02	102	34	0.0116
0.03	123	29	0.056
0.04	125	31	0.069
0.05	138	31	0.066

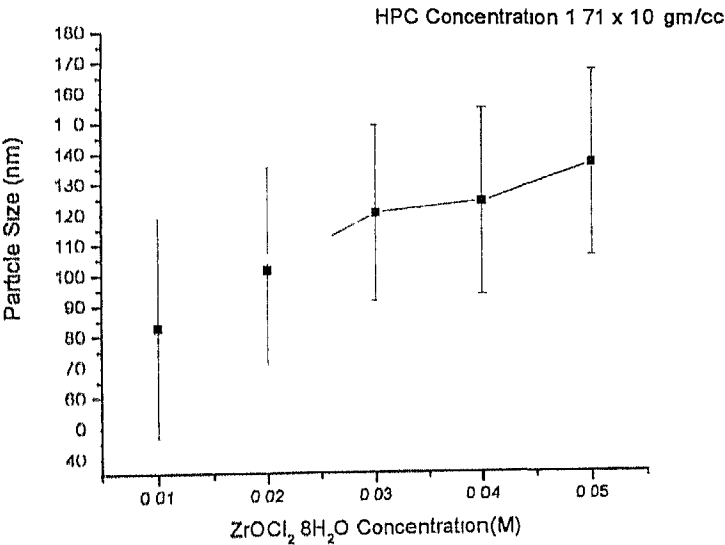


Figure 3.2 Particle Size of hydrous zirconia in mother liquor as a function of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration at a fixed HPC concentration ($1.71 \times 10^{-3} \text{ gm/cc}$)

Table 3.3 pH of the as prepared suspension

ZrOCl ₂ 8 H ₂ O Concentration (M)	pH
0.01	2.4
0.02	2.1
0.03	1.68
0.04	1.55
0.05	1.43

In the previous work a somewhat higher particle size value of the as prepared suspension was reported. This may be due to the lower pH of the mother liquor during the particle size measurement in the present case (Table 3.3). It was changed to 7.8 in the earlier work. The high acidity of the mother liquor helps in degradation of polymeric form of hydrous zirconia thereby reduces the particle size value to some extent.

3.2.3 Effect of ultrasonication in reducing the particle size of hydrous zirconia in mother liquor

Ultrasonication plays some roles in dispersing the particles and thereby reducing the measured particle size as is evident from the Table 3.4.

Table 3 5(a) Variation of particle size of hydrous zirconia from precursor concentration of 0.01 M ($\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$) with various time interval measured by HPPS

Sl No	Time interval (min)	Particle Size (nm) HPPS	
		Average diameter	Average width
1	10	91	51
2	180	91	15
3	190	89	21
4	235	85	25
5	835	86	33
6	900	94	36
7	960	102	35
8	1380	99	51

Table 3 5(b) Variation of particle size of hydrous zirconia from precursor ($\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$) concentration of 0.1 M with various time interval measured by HPPS

Sl No	Time interval (min)	Particle Size (nm) HPPS	
		Average diameter	Average width
1	15	415	166
2	45	454	190
3	75	353	129
4	140	282	149

The particle size of hydrous zirconia suspension prepared from low precursor concentration (0.01 M) remains unaltered for very long duration compared to that prepared from high precursor concentration (0.1 M) the latter shows clear sign within 2 hrs of time preparation. After 2 hours the suspension was clear instead of usual milky white. This indicates that within two hours the particles have dissolved and acquired a very low size. The size of 282 nm measured after 140 minutes is because of the usual presence of a few large dust particles. From the dissolution characteristics of the hydrous zirconia suspension it is evident that suspension with higher pH remains stable over long range of time but the suspension with lower pH dissolves readily within very short period of time. This may be because of the presence of higher concentration of H^+ in case of lower pH suspension that effectively breaks away the oxygen bridges in hydrous zirconia and helps in dissolution of the same.

3.4 Particle size variation in the dried powder

Drying is a very critical stage in case nano powder synthesis. To get fine dried nano powders it should be well dispersed in proper solvent before drying at optimum temperature to prevent agglomeration. The alcohol washed precipitate was further diluted with isopropyl alcohol and dispersed by ultrasonication for long time. The well dispersed alcoholic suspension was poured in a large flat Petri dish and dried in an oven at $90^\circ C$ for 6 hours. Powders were prepared by varying the concentration of $ZrOCl_2 \cdot 8H_2O$ from 0.01 M to 0.05 M at a fixed HPC concentration of 1.71×10^{-3} gm/cc. Table 3.6 the particle size of undoped hydrous zirconia powders prepared from different $ZrOCl_2 \cdot 8H_2O$

concentration and variation of particle size with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentrations has been depicted in figure 3.3

Table 3.6 Particle Size of the dried powder (undoped hydrous zirconia) measured by HPPS after redispersion in propanol

Concentration of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (M)	Diameter (nm)	Width (nm)	PDI
0.01	114	60	0.400
0.02	125	58	0.359
0.03	181	52	0.453
0.04	221	58	0.352
0.05	226	62	0.347

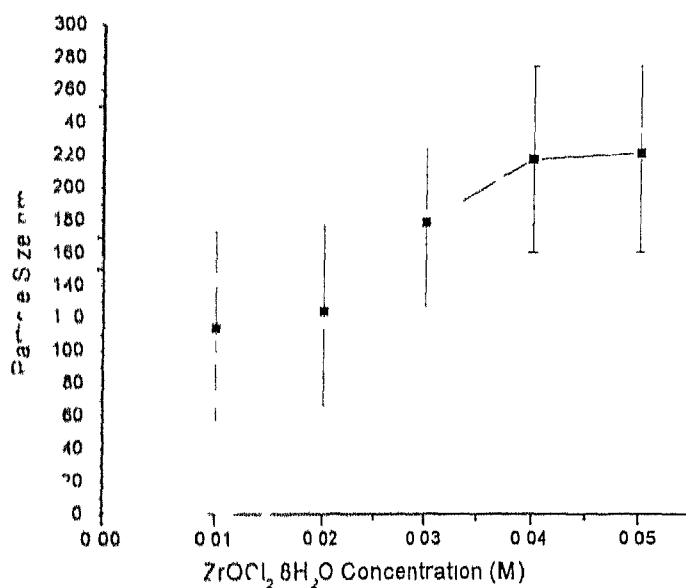


Figure 3.3 Particle Size of hydrous zirconia dried powder as a function of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration at a fixed HPC concentration (1.71×10^{-3} gm/cc)

As expected the particle size values of the dried powder increases with increase in the precursor ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) concentration. The particle size of the dried powder is nearly 40% higher than that of as prepared particles of hydrous zirconia in the suspension (Table 3.2). This is most likely due to the agglomeration of the particles during the drying process. These agglomerate separately do not break during redispersion for particle size measurement. The higher polydispersity index (0.35 to 0.45 Vs 0.01 to 0.07) also supports this conclusion.

The Gd_2O_3 doped zirconia powders has been prepared by the same method as the undoped powder as described in section 2. Table 3.7 shows the values of particle size of the doped powders prepared from different precursor ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) concentration. Figure 3.4 gives the variation in particle size value with change in $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration for doped powders.

Table 3.7 Particle size of the 10 mol% Gd_2O_3 doped ZrO_2 as prepared dried powders

Concentration of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (with 10 mol% Gd_2O_3) (M)	Diameter (nm)	Width (nm)	PDI
0.01	115	63	0.250
0.02	119	57	0.122
0.03	174	55	0.398
0.04	208	57	0.340
0.05	224	61	0.374

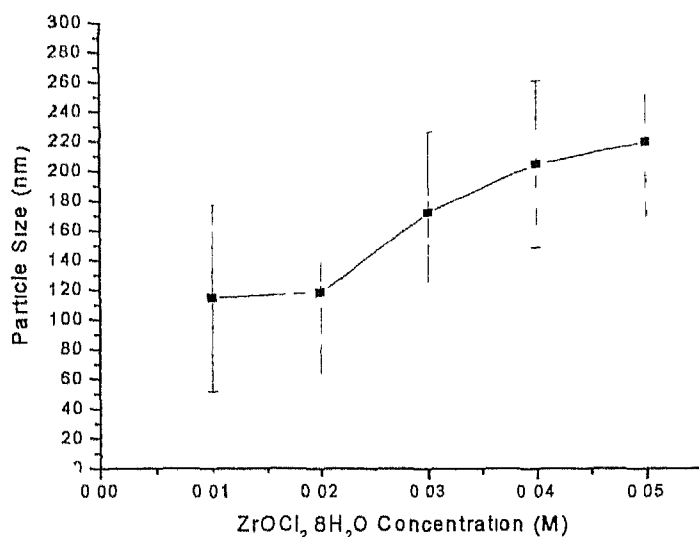


Figure 3.4 Particle Size of doped (10 mol% Gd₂O₃) zirconia dried powder as a function of ZrOCl₂·8H₂O concentration at a fixed HPC concentration (1.71 × 10³ gm/cc)

From the particle size data of both doped (Table 3.7) and undoped (Table 3.6) dried powders it is evident that the particle size values in two cases do not vary much. That is to say that presence of 10 mol% Gd₂O₃ does not affect the solubility of ZrOCl₂ in the alcohol water system during cooling to 3^o C and subsequent heating to nearly 80^o C.

3.5 Surface area of dried powder

The BET surface area of the amorphous dried powders was measured by using a COULTER SA3100 instrument. The surface area measured for 10 mol% Gd₂O₃ doped ZrO₂ powders prepared from different ZrOCl₂·8H₂O concentration but at a fixed HPC concentration of 1.71 × 10³ gm/cc has been given in Table 3.8. The hydrous zirconia powders are not calcined and a certain amount of HPC (Hydroxy Propyl Cellulose) are

attached to the particle surface. So the density of the amorphous dried powder will be much lower than the theoretical density of zirconia ($\sim 6 \text{ gm/cc}$). Taking a density of dried powder to be nearly 50% of the theoretical density of zirconia, the particle size values of powders are calculated from BET surface area. Particle size of the dried powders as measured from the BET surface area is much lower than those obtained from HPSS measurement or TEM observation. This may be explained by the fact that the particles observed in the TEM micrograph are made of smaller elementary particles and the particle surface being porous, the inert gas used for BET surface area measurement enters the surfaces between the elementary particles, resulting in a much higher surface area and consequently a much lower particle size of the dried powder. As shown later, the elementary particle size from BET surface area is nearly equal to the crystallite size determined by X-ray diffraction line broadening.

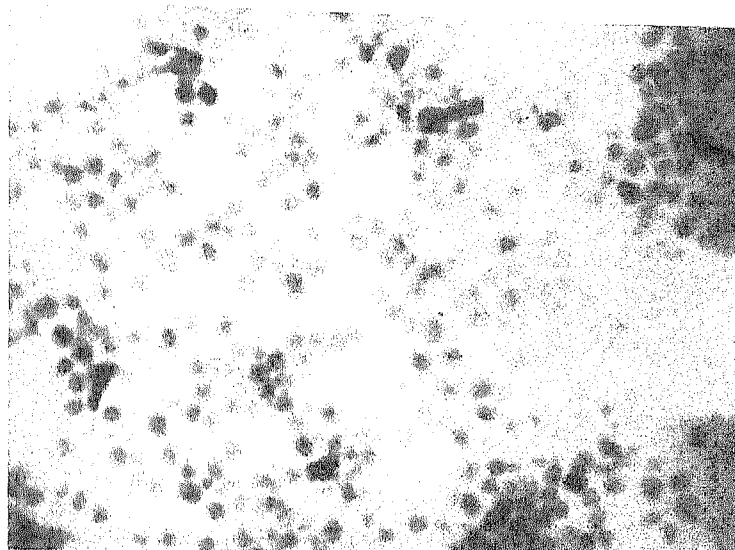
Table 3.8 Measurement of BET surface area of the as prepared dried powder

ZrOCl₂ · 8 H₂O (M)	Surface area (m²/gm)	Particle size (nm)
0.05	138	12
0.04	264	8
0.01	309	6

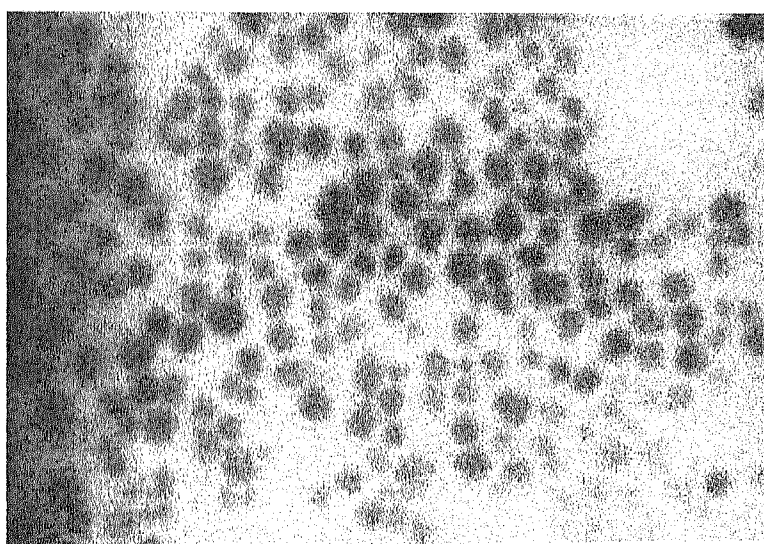
3.6 TEM observations of hydrous zirconia particle in mother liquor and dried state

To observe the particle morphology and dispersity of the hydrous zirconia particle in mother liquor and after drying, the hydrous zirconia samples were characterized using

TEM. The detailed sample preparation and characterization technique has been described in section 2.



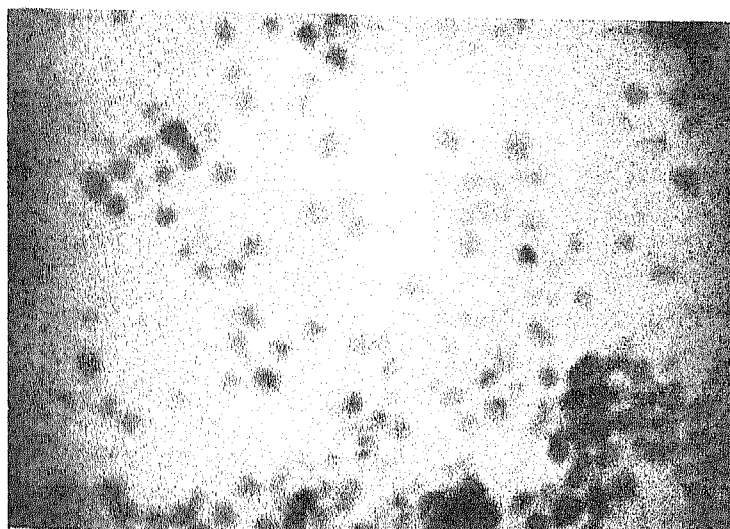
(a) 150 nm



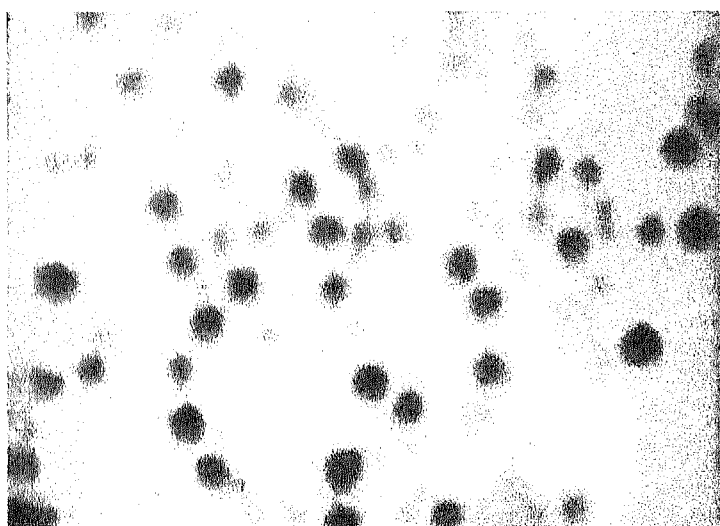
(b) 150 nm

Figure 3.5 : TEM micrographs of hydrous zirconia particle in mother liquor prepared from (a) 0.01 M and (b) 0.02 M $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$.

Figure 3.5 (a) and 3.5 (b) are the TEM micrographs of hydrous zirconia in mother liquor prepared from 0.01 M and 0.02 M $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$ respectively. The micrographs show a well dispersed suspension of hydrous zirconia particle in mother liquor.



(a) 120 nm



(b) 120 nm

Figure 3.6: TEM micrograph of the dried hydrous zirconia powder (dispersed in isopropanol) prepared from (a) 0.01 M and (b) 0.02 M $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$.

One of the main challenges in nano particle synthesis is to get dried nano powders in unagglomerated form. Figure 3.6 (a) and 3.6 (b) show the TEM micrograph of the dried hydrous zirconia powder (dispersed in isopropanol) prepared from a precursor concentration of 0.01 M and 0.02 M $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$ respectively. From these figure it is evident that the dried powders can be redispersed in isopropanol.

During washing of hydrous zirconia particle some HPC molecules are also removed from the particle surface. As there is not sufficient coverage by HPC molecule in the dried hydrous zirconia particles they may join together through the uncovered particle surface and form a chain like structure as depicted in figure 3.7.

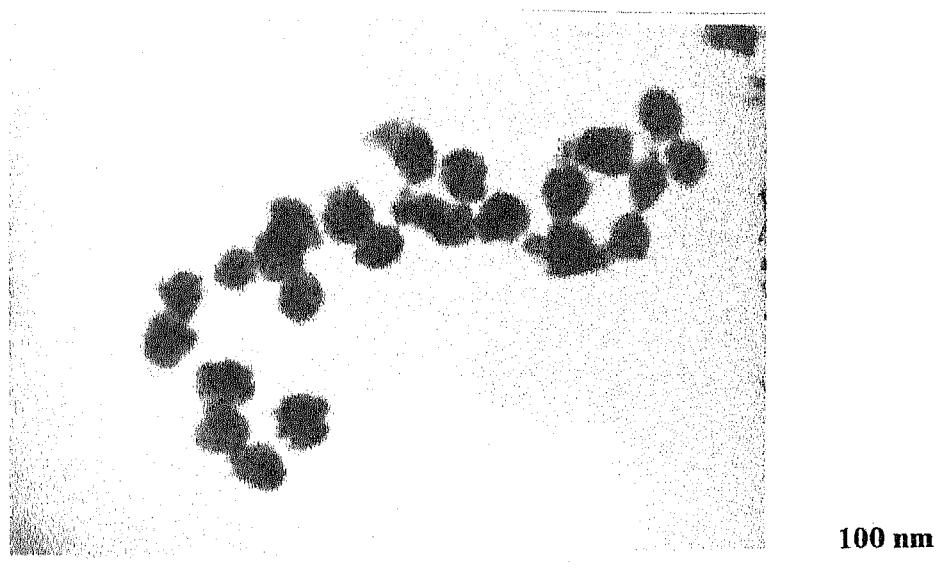


Figure 3.7: TEM micrograph of the dried hydrous zirconia powder (dispersed in isopropanol) prepared from 0.03 M $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$.

3.7 Two step preparation of particles to obtain narrow size distribution

Monodisperse powders or powders with very narrow size distribution are very useful in the sense that they give a high packing density and thus a very good green and sintered

density Hydrous zirconia powder prepared via one step process by microwave heating for 20 seconds at 80% microwave power show particles with fairly large size distribution [Fig 3.9 (i)] To minimize the polydispersity of the powders and to obtain powders with narrow size distribution two steps heating process was adapted as described in chapter 2. In the first step nuclei are produced by heating the precursor solution for a short time. In the second step the suspension is aged at a lower temperature of 50° C to allow controlled growth of the particles. The results obtained for different experiments are tabulated below.

Table 3.9 (a) Particle size variation of hydrous zirconia for heat treatment of 5 seconds at 80 % microwave power

Precursor	Microwave treatment	Processing condition	Holding Temp ^o C)	Holding Time (hr)	Particle size (nm)	Width (nm)
0.01M ZrOCl ₂ · 8H ₂ O IPC 1.71 X 10 ⁻³ gm/cc	At 80% power for 5 second	Cooling to 3° C and then microwave heating (no filtration)	25	0	167	100
			50	1.5	87	150
			50	2.5	91	110
			50	3.5	93	110
			50	6	93	20
			50	7	88	20
			50	8	87	15
			50	9	89	15

The particle size value measured after nucleation at 80% microwave power for 5 seconds i.e. at zero holding time is quite high and decreases with the holding time [Table 3.9 (a)]. This unusual result is an artifact. This arises because at zero or short times the actual particle size is quite small and is overwhelmed by the presence of a few larger dust particles as described earlier. With increasing holding time at 50 °C the initially formed nuclei grow and begin to dominate the contribution from the dust particles. Hence there is a decrease in the measured particle size. The purpose of this two steps process was to obtain a narrow particle size distribution. This objective is fulfilled. Another important observation is that with increasing aging time the particle size distribution becomes narrower and after 8 hours the width in the particle size distribution is only 15 nm.

TEM micrographs from the drops of mother liquor dried on TEM grids are shown in figure 3.8 (a-d). The particle size just after the nucleation step is quite small ~ 12 nm (fig 3.8 (a)). The particle size increases with aging time. Thus it is nearly 28 nm, 38 nm and 47 nm after aging times of 1.5 hrs, 6 hrs and 8 hrs respectively. The narrowness of the particle size distribution is not so apparent from their figure especially that at higher aging times, but in the HPPS data it is unmistakable.





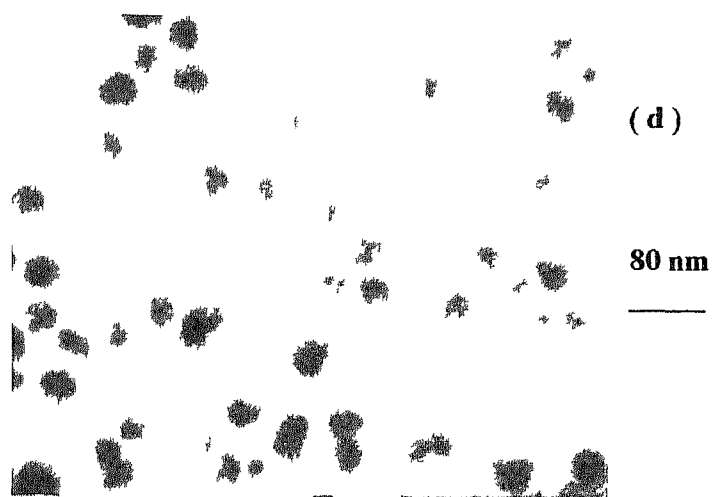


Figure 3.8 TEM micrographs from the drops of mother liquor dried on the TEM grids after (a) nucleation (b) 1.5 hrs of aging (c) 6 hrs of aging and (d) 8 hrs of aging

Table 3.9 (b) Particle size variation of hydrous zirconia for heat treatment of 10 seconds at 80 % microwave power

Precursor	Microwave treatment	Processing condition	Temp ^o C	Holding Time (hr)	Particle size (nm)	Width (nm)
0.01M ZrOCl ₂ · 8H ₂ O H ₂ O HPC 1.71 X 10 ⁻³ gm/cc	At 80% power for 10 second	Cooling to	10	0	156	150
		3 ^o C and	50	1	103	20
		filtered	50	2	109	20
		before	50	4	109	50
		micro	50	6	114	50
		wave heating	50	7	115	50

To minimize the error in the particle size value due to the presence of dust particle the same experiment was conducted by filtering the precursor solution through the 0.2 micron filter prior to the microwave treatment at 80% power for 10 seconds. But yet the particle size after the nucleation stage was quite high (Table 3.9 b). This is to say that it is very difficult to eliminate the influence of dust particle in the particle size value measured by HPPS instrument. Here the particle size value after aging at 50° C is little bit higher compared to the previous case and the width becomes narrower (20 nm) within 1 hour of aging at 50° C. After 4 hours of aging time the width in the particle size distribution again increases (50 nm). The larger size is due to longer heat treatment (viz 10 seconds Vs 5 seconds) in the first step.

Table 3.9 (c) Particle size variation of hydrous zirconia for heat treatment of 1.5 seconds at 100 % microwave power

Precursor	Microwave treatment	Processing condition	Tempr (° C)	Holding Time (hr)	Particle size (nm)	Width (nm)
0.01M ZrOCl ₂ · 8H ₂ O HPC 1.71 X 10 ⁻³ gm/cc	At 100% power for 15 second	Cooling to 3° C and filtered before micro wave heating		0		
			12	1	165	80
			50	2	109	20
			50	3	112	20
			50	4.5	111	25
			50	7	109	100

Table 3.9 (c) shows the results for the case when the initial microwave treatment was carried out for 15 seconds with 100% microwave power. Table 3.9 (c) indicates that the particle size values are higher than those at Table 3.10(a) but smaller than at Table 3.9 (b) and width becomes narrower (20 nm) within 1 hour of aging at 50⁰ C but it increases with increase in the aging time. The increase in width of the distribution after 7 hours of aging is not understood.

Comparing the above three methods for producing particle with narrower size distribution it can be concluded that for an initial heat treatment of 80 % microwave power for 5 seconds and aging at 50⁰ C gives a particle size with very narrow width (15 nm) even after 9 hours of aging at 50⁰ C and the particle width keeps on decreasing with increase in aging time. For all other cases the width in the particle size distribution increases after certain time of aging. So heating the precursor at 80 % microwave power for 5 seconds and then aging at 50⁰ C for long hours is the best way of producing nano particle of hydrous zirconia with very narrow size distribution. Figure 3.10 compares the particle size distribution between one step and the two steps process. The distribution for the two steps process [figure 3.9(b)] is much narrower (15 nm) compared to that (37 nm) in one step process [figure 3.9(a)].

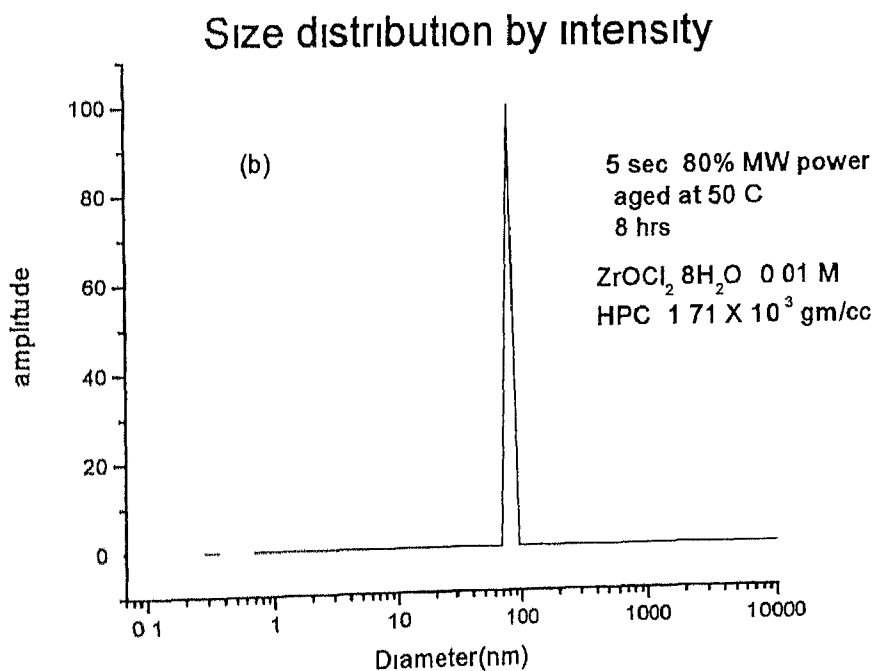
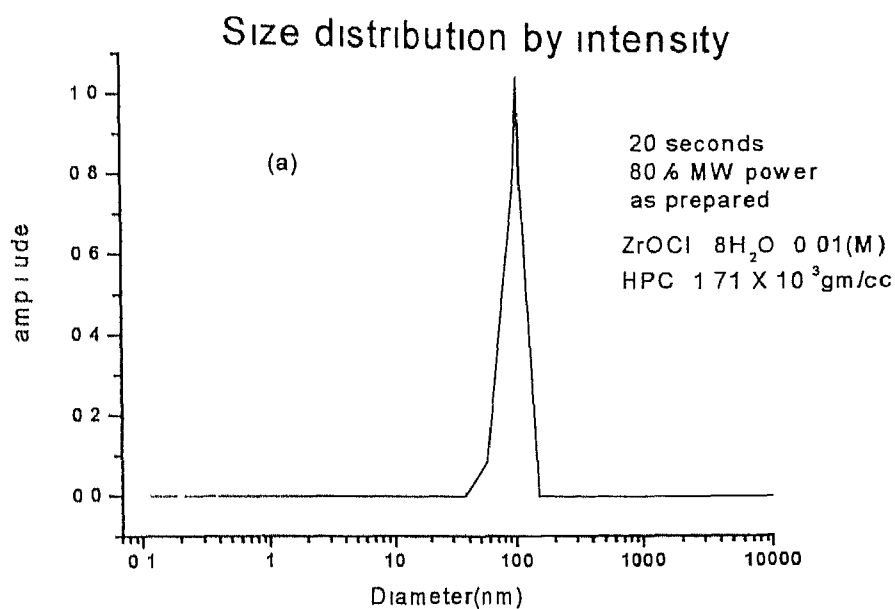


Figure 3.9 Size distribution of hydrous zirconia prepared by (a) single step process
(b) by the two steps process

Hydrous zirconia prepared via two steps process that is first nucleation at 80% microwave power for 5 seconds and then aging at 50 ° C upto 8 hrs shows a very narrow particle size distribution whereas the single step treatment by 80 % microwave power for 20 seconds produces hydrous zirconia with wider particle size distribution. This may be explained by the fact that in single step process the nuclei form over a period of time and thereby the growth occurs in some nuclei much earlier than in the other nuclei during 20 seconds of heat treatment resulting in hydrous zirconia with wider particle size distribution. In case of the two steps process nucleation occurs for a shorter period of time (for 5 seconds) and then nuclei grow on aging at 50° C. So growth time from nuclei to nuclei does not vary too much and that gives a hydrous zirconia particle size with narrower width.

3.8 Modification of the surface of Gd₂O₃ doped ZrO₂ particle

When an oxide particle is suspended in water its surface gets charged



The net charge on the particle surface can be negative or positive depending on the pH. The pH at which the net charge is zero is called the point of zero charge (ZPC). At a pH other than ZPC the net charge on the particle surface causes the concentrations of the counterions to be in excess of the average concentration of ions in the liquid. This excess of counterions is distributed in a diffuse layer the concentration decreasing as one moves away from the particle surface and becoming equal to average value at larger distances. These layers of excess of counterions together with the charge on the particle surface

constitute an electrical double layer. Because of the charge on the particle surface and its screening by the diffuse electrical double layer, a potential develops on the particle surface which decreases exponentially as one moves away from the particle surface. The potential at the particle surface can not be measured, but the potential at a distance at which the particle and adhering liquid layer shears away from the rest of the liquid when the particles move can be measured. This is called the zeta potential.

The zeta potential values of 10 mol% Gd_2O_3 powders of particle size of 115 nm were measured with variation of pH of the suspension by calculating the mobility of the particles under an externally applied electrical field.

Table 3.10 Zeta potential values of Gd_2O_3 doped ZrO_2 at different pH

Sample	pH	Zeta Potential (mV)
10 mol% Gd_2O_3 doped ZrO_2 (prepared from 0.01 M $ZrOCl_2 \cdot 8H_2O$ and 1.71×10^{-3} gm/cc HPC)	2	36.5
	3	30.06
	4	15.9
	5.5	11.4
	6	18
	7	26

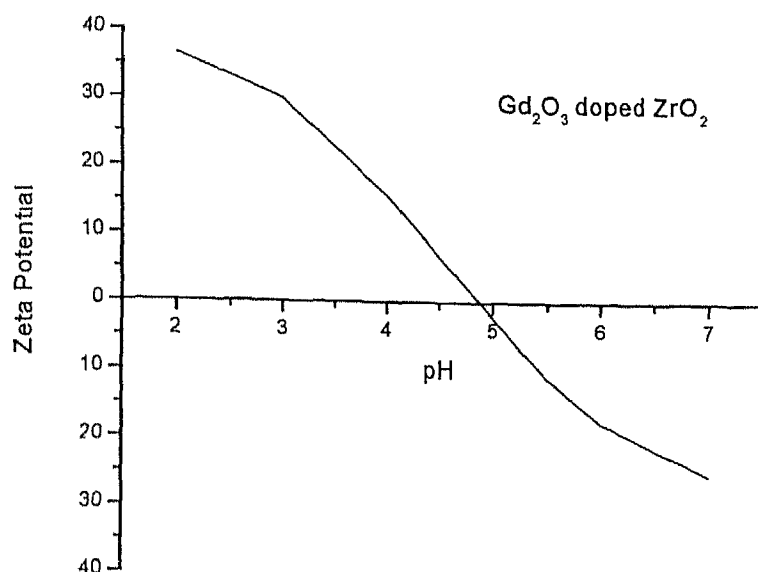


Figure 3 10 Variation of zeta potential as a function of pH

It is evident from the fig 3 10 that with increase in pH the zeta potential value decreases and then gets reversed and becomes more negative with increase of pH. At pH ~ 4.8 the zeta potential becomes zero and it is denoted as the isoelectric point of 10 mol% Gd_2O_3 doped ZrO_2 . At lower pH (below 4.8) the zirconia particles are positively charged and form diffuse electric double layer with negatively charged gegen ions. As the pH increases the electric double layer width also decreases as the positive charge density on the hydrous zirconia particle surface is decreased and so the value of zeta potential decreases. If the pH is increased beyond the isoelectric point (here 4.8) the charge on the particle size surface gets reversed and it forms a electric diffuse double layer with

positively charged gegen ions. With further increase in pH the density of negative charge on the hydrous zirconia particle surface increases and thus the thickness of the diffuse electrical double layer gets enhanced and as a result the zeta potential value rises.

3.8.1 Silica Gel coating on Particles of Zirconia

The growth of a silica layer on zirconia particle suspended in TEOS sol has been measured by observing the changes in the zeta potential of zirconia particles with respect to time. Table 3.11 presents the data of zeta potential values obtained after different time intervals and figure 3.11 shows the variation in zeta potential with respect to time.

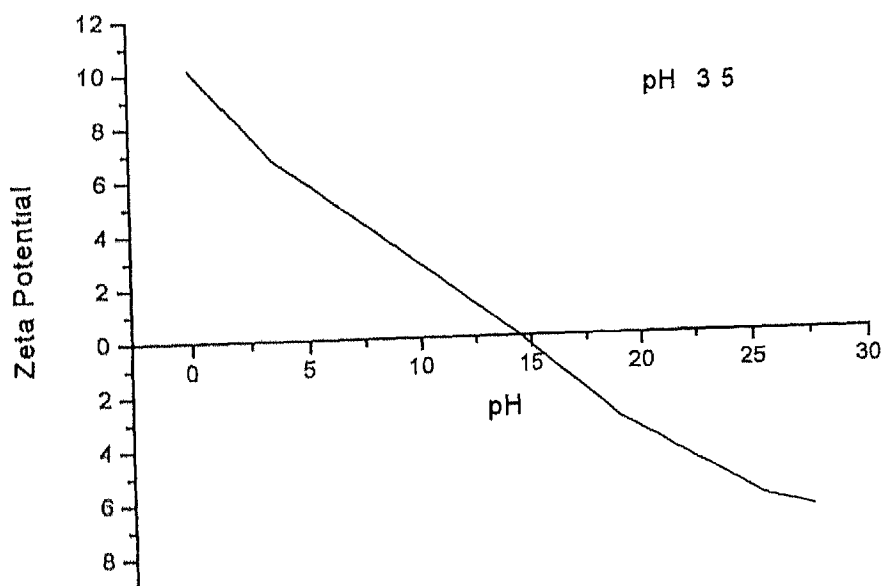


Figure 3.11 Change of zeta potential as a function of time

Table 3.11 Zeta potential values of Gd₂O₃ doped ZrO₂ after different times interval at a fixed pH of 3.5

Time (hrs)	Zeta Potential (mV)
0	10.2
3.5	6.8
14.5	0
19	3.1
25.5	6.3
27.5	6.7

At the initial stage (time $t=0$) the zeta potential of the particles show a high positive value close to the value of zeta potential of pure Gd₂O₃ doped zirconia at that pH. With time zeta potential values gets decreased and becomes zero at 14.5 hours then starts to be negative with increase in aging time. At 27.5 hours it shows a negative value of zeta potential that is close to the zeta potential of silica at that pH.

The isoelectric point of zirconia is 4.8 whereas that of silica is 2. The suspended zirconia particle in H₂O sol of pH 3.5 was positively charged whereas the silica gel that is generated from H₂O in due course of aging is negatively charged at pH 3.5. So silica gel is deposited on the zirconia particle surface by the electrostatic force of attraction. When there was no silica gel layer on the zirconia surface a positive zeta potential value was observed and as the silica gel started depositing on the zirconia particle surface the zeta potential started decreasing, got reversed and then approached the zeta potential value of silica at long times (27 hours).

The formation of the silica film changes the zeta potential of the particles with time from the value corresponding to ZrO_2 surface at pH 3.5 to the value for silica surface at the same pH. It takes some time (almost 27 hrs) for this zeta potential value of the suspended particle to reach that of silica, suggests that silica film forms by nucleation and growth mechanism on zirconia particle surface.

3.9 Particulate composite films by sol gel

It is very difficult to obtain crack free thick film by sol gel method because during drying and subsequent heat treatment a thick film gets cracked due to differential shrinkage between different parts of the gel film and because of the constraints of the substrates. By sol gel method thick films are usually obtained by multilayer coating with some heat treatment between each coating. Upwards of 20 coatings and heat treatment steps may be required to obtain a 1 μm thick film. Introduction of particles of second phase can significantly increase the toughness of the gel film and thereby enhance its resistance to crack growth and propagation during heat treatment. Here we have introduced a well dispersed suspension of ZrO_2 , Al_2O_3 and SiO_2 particle to a polymeric silica solution (TEOS sol). TEOS sol was sufficiently (0.5 day, 1 day, 2 days) aged so that a long polymeric network of SiO_2 can be formed and then the second phase particles were added to the aged sol. A surfactant hydroxyl propyl cellulose (HPC) was used in different amount (0.002×10^{-3} gm/cc to 0.008×10^{-3} gm/cc) to disperse the second phase particle in isopropanol. These second phase particles interact with polymeric SiO_2 network to form different kinds of flocs, clusters, chains in the gel.

Figure (3.13) and figure (3.14) show the SEM micrograph of SiO_2 - ZrO_2 composite film where the second phase particle (ZrO_2) was dispersed in isopropanol - HPC solution.

with a HPC concentration of 0.002×10^{-3} and 0.004×10^{-3} gm/cc respectively. Highly concentrated flocs in gel matrix are seen in figure 3.14 whereas figure 3.13 represents some small clusters of particles oriented randomly in the composite film.

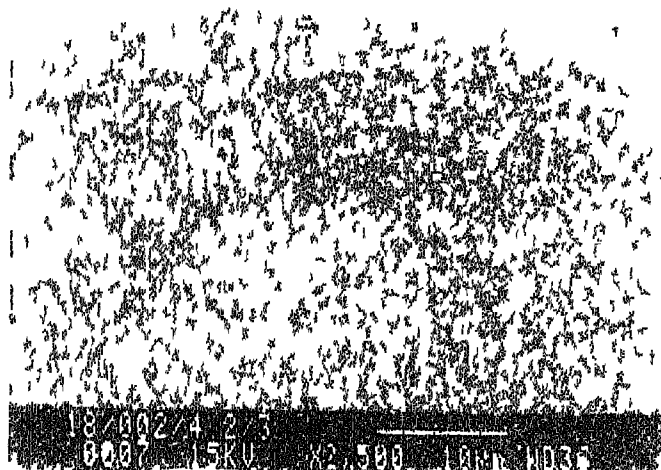


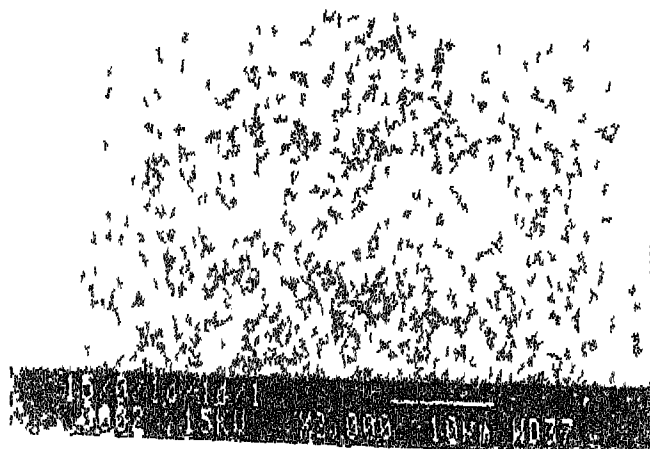
Figure 3.13 SEM micrograph of SiO_2 - ZrO_2 composite film at HPC concentration of 0.002×10^{-3} gm/cc



Figure 3.14 SEM micrograph of SiO_2 - ZrO_2 composite film at HPC concentration of 0.004×10^{-3} gm/cc

The particle distribution and arrangement in the SiO_2 - ZrO_2 [(3.15 (a))] and SiO_2 - Al_2O_3 [(3.15 (b))] composite film has been shown below where no HPC was used as a

surfactant to disperse the second phase particle ($\text{ZrO}_2 - \text{Al}_2\text{O}_3$) in isopropanol. Both figure 3.15 (a) and 3.15 (b) represent highly concentrated flocs in the gel matrix.



(a)

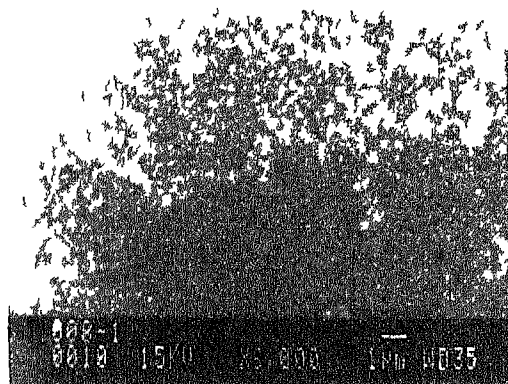


(b)

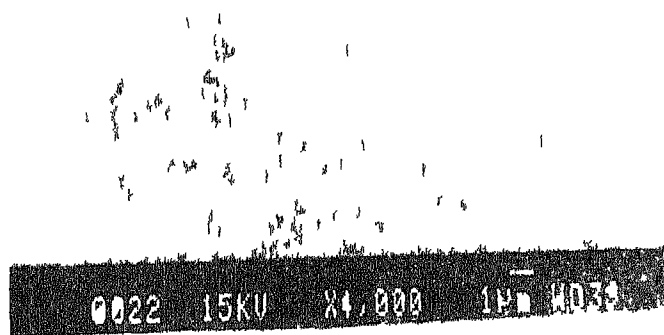
Figure 3.15 SEM micrograph of (a) $\text{SiO}_2 - \text{ZrO}_2$ and (b) $\text{SiO}_2 - \text{Al}_2\text{O}_3$ composite film at zero HPC

A somewhat interesting trend in particle arrangement is observed when the second phase particle is dispersed in isopropanol HPC solution containing 0.008×10^{-3} gm/cc HPC.

Figure 3.16 (a) and 3.16 (b) show the particle arrangement in the composite film where 0.008×10^{-3} gm/cc HPC was used to disperse TOSOH zirconia ($0.2 \mu\text{m}$) and hydrous zirconia ($0.15 \mu\text{m}$) particles respectively. Figure 3.16 (a) shows some chain and ring like arrangement of particulate matter in the gel matrix. A thick chain of particles is seen in figure 3.16 (b).



(a)



(b)

Figure 3.16 SEM micrograph of (a) $\text{SiO}_2 - \text{ZrO}_2$ (TOSOH) and (b) $\text{SiO}_2 - \text{ZrO}_2$ (hydrous) composite film at 0.008×10^{-3} gm/cc HPC

The uncalcined hydrous zirconia powder contains some HPC molecules adsorbed onto particle surface which may affect the particle arrangement that is different from the one obtained by using TOSOII zirconia as a second phase particle

From all these SFM micrographs it can be said that second phase particle dispersed with lower amount of HPC (0.002×10^{-3} - 0.004×10^{-3} gm/cc) give clusters and flocs that are distributed randomly in the gel matrix. Particle having no HPC as a dispersant also produces large concentrated flocs. Some long chains and rings of particles are seen when second phase particles are dispersed in isopropanol 0.008×10^{-3} gm/cc HPC solution.

However this correlation is only tentative based on a few experiments. Many more experiments and more carefully controlled conditions need to be carried out to establish the correlation between the process parameters and the arrangement of particles obtained.

A remarkable observation in all the films was that the films despite having significant thickness were not cracked except at the periphery of the dried drop. Figure 3.17 shows the profilometer traces of a dried drop. The thickness of most of the film is $0.25 \mu\text{m}$ [3.17 (a)] while at the periphery it is about $3.5 \mu\text{m}$ [3.17 (b)].

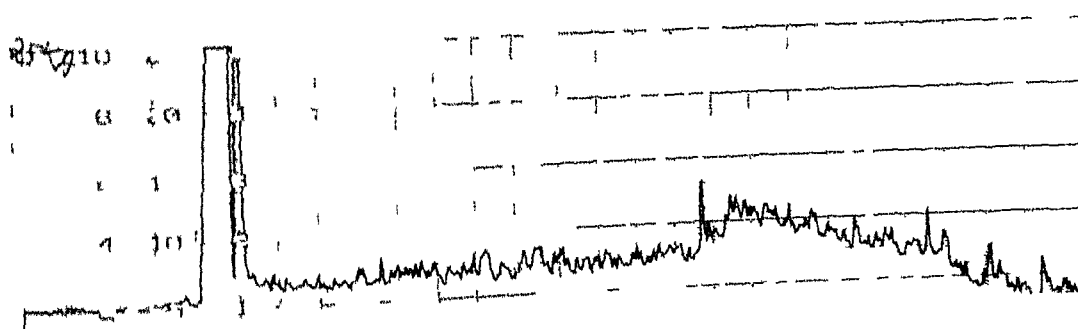


Figure 3.17 (a) full scale length 25 KA⁰

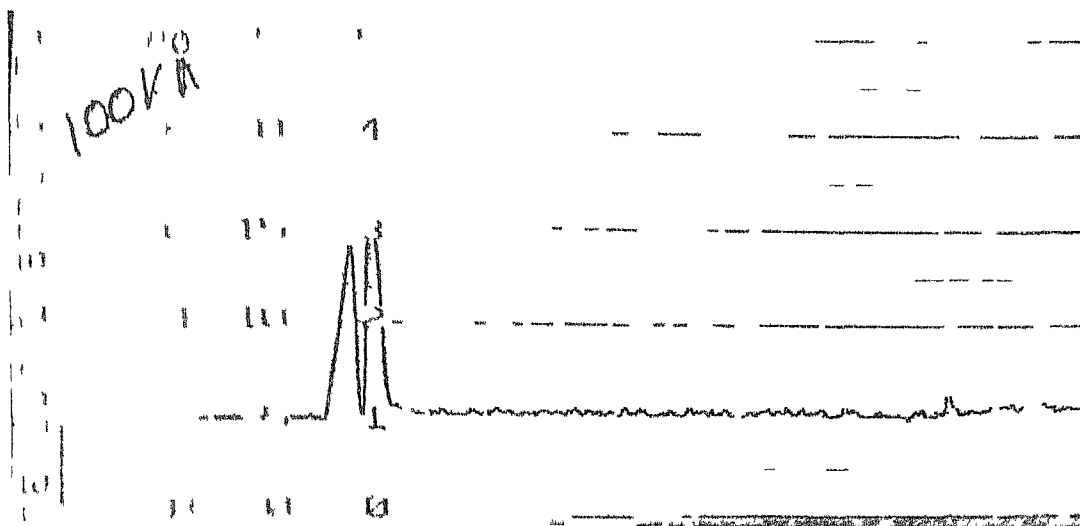


Figure 3 17 (b) full scale length 100 KA⁰

Figure 3 17 Thickness profile of SiO₂ ZrO₂ composite film at (a) central region and (b) peripheral region

At the periphery more liquid migrates due to capillary forces resulting in increased thickness. In all the figures shown before the gel phase is untracked. Another example is shown in figure 3 18



Figure 3 18 Uncracked region of a film in presence of secondary particle

On the other hand in the region where the particle density is low the film is invariably cracked (Figure 3 19)



Figure 3 19 Cracked Structure of a film prepared by sol gel method There is no particle in the film in this region

3 10 Crystallization of dried powder

One of the important characterization techniques of nano powders is to evaluate different phases by crystallizing the powders at different temperature and to see the changes in crystallite size with variation in temperature and its influence on the phase composition. In the present study amorphous powders were crystallized by calcination to different temperature for 1 hour.

3 10 1 Phase analysis by X ray diffraction

X ray diffraction technique is used to determine the phases present in the undoped and doped zirconia powder by heating the powders at 600⁰ C and 900⁰ C for 1 hour. The X-ray diffractograms (intensity Vs 2 θ) of the powders 2 θ values were varied from 20⁰ to

80⁰ The values of 2θ corresponding to the peaks obtained from the diffraction patterns are noted and compared with the standard data. Figure 3.20 shows the XRD plots of undoped zirconia powders crystallized at 600⁰ C for 1 hr.

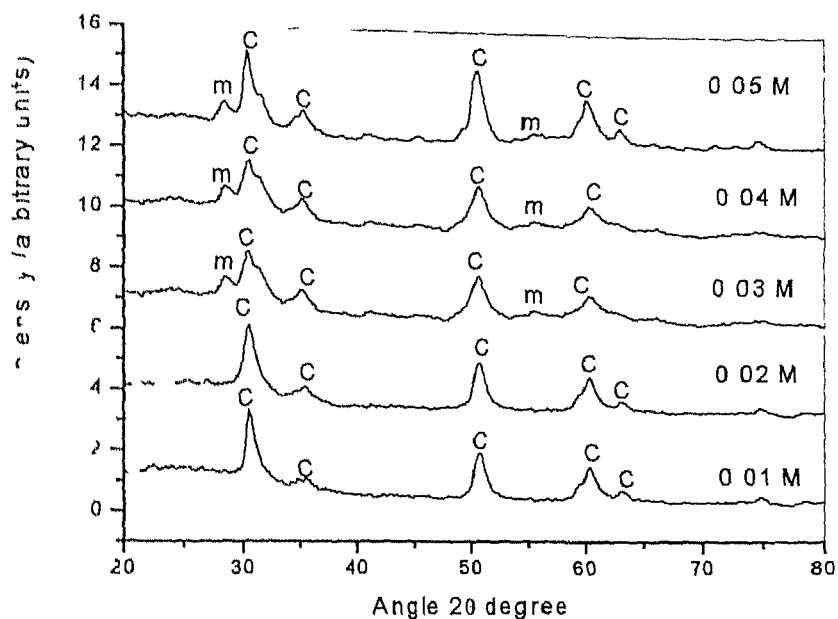


Figure 3.20 X ray diffraction plots of undoped zirconia powders heat treated at 600⁰ C / 1 hr

The phases present in crystallized powder prepared from different ZrOCl₂·8 H₂O concentration and the corresponding values of crystallized size have been given in table

3.12

Table 3.12 Phase characterization of undoped Zirconia powders prepared from different precursor concentration after heating at 600° C/ 1hr

Precursor Concentration $ZrOCl_2 \cdot 8H_2O$ (M)	Phases	Crystallite size Calculated from cubic peak at 60°
0.01	c	8
0.02	c	8
0.03	c + m	9
0.04	c + m	10
0.05	c + m	10

The powders prepared from 0.01 M and 0.02 M precursor show only cubic phase at 600° C which may be attributed to the small particle size in this powder. Small particle size that stabilizes the metastable cubic phase at room temperature. On the other hand the powders prepared from higher precursor concentrations (0.03, 0.04, 0.05 M) show both cubic and monoclinic phases after heat treatment at 60° C due to larger particle size.

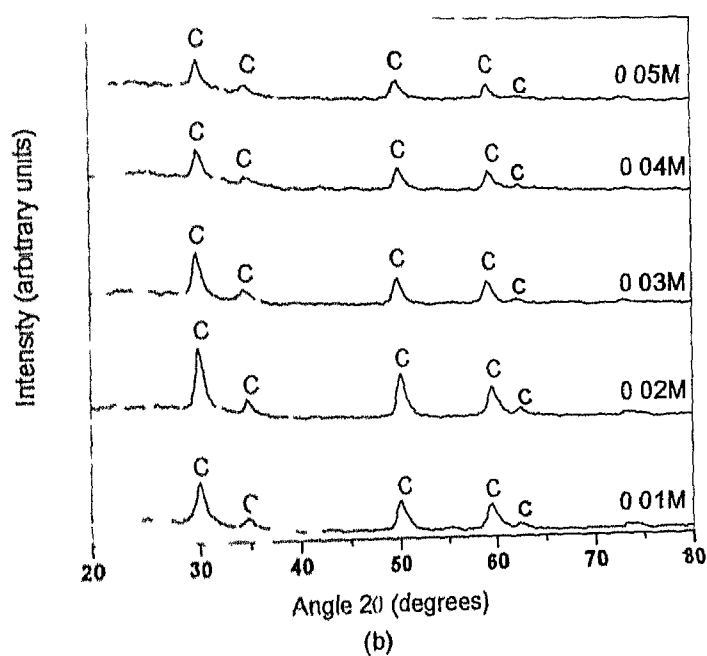
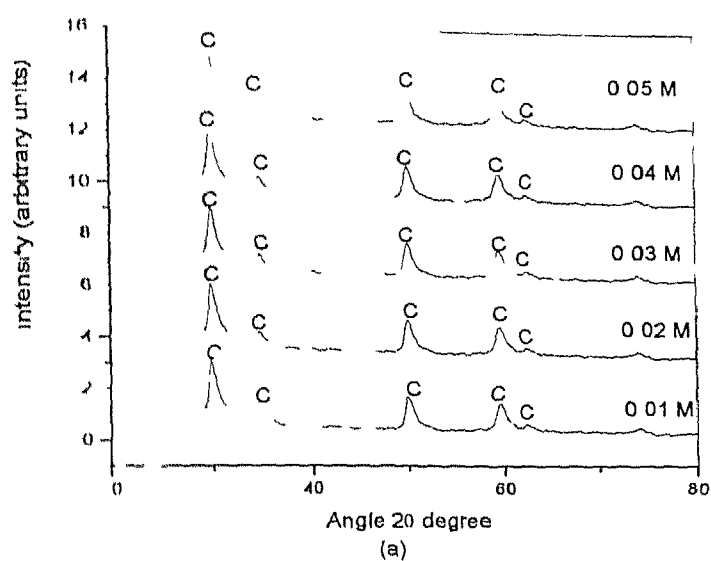


Figure 3 21 X ray diffraction plots of 10 mol% Gd_2O_3 doped zirconia powders heat treated at (a) $600^\circ C/1\text{ hr}$ and (b) $900^\circ C/1\text{ hr}$

Figure 3.21 (a) and 3.21 (b) show the XRD plots of 10 mol% Gd_2O_3 doped zirconia powders crystallized at 600°C and 900°C for 1 hr respectively. 10 mol% Gd_2O_3 doped ZrO_2 powders prepared from different $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration (0.01 M to 0.05 M) show only c phase throughout the temperature range from 600°C to 900°C . All the Gd_2O_3 doped powders crystallized at 600°C for 1 hr have a crystallite size of ~ 8 nm whereas that for 900°C / 1 hr heat treated sample is ~ 9 nm. Thus it is evident that crystallite size does not vary too much with the change in $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration and is independent of the precursor concentration. Also it can be said that HPC has no role to play in nucleation only it can alter the subsequent growth process which is reflected in the different particle size value for different ZrOCl_2 precursor concentration. The fact that in case of 10 mol% Gd_2O_3 doped sample the primary crystallite size does not increase too much on heating from 600°C to 900°C is very encouraging and we can hope for a sintered body from this powder with a grain size in very low nano range.

CHAPTER 4

SUMMARY AND CONCLUSIONS

The present work was undertaken with several aims first to prepare both undoped and Gd_2O_3 doped zirconia nano powders with narrow size distribution secondly to modify their surface characteristics by sol –gel technique and thirdly to use them as a second phase toughening agent to obtain crack free thick films by sol gel method

Both 10 mol% Gd_2O_3 doped and undoped zirconia nano powders were prepared by homogeneous precipitation technique of heating alcohol water solution containing zirconyl chloride salt and hydroxypropyl cellulose (used as a surfactant) It was found that the molar concentration of ZrOCl_2 has a direct effect on the particle size of hydrous zirconia The particle size can be controlled by suitably selecting the initial concentration of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ Particle size of the dried powder (as measured by HPPS) varies from 115 nm to 225 nm as $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration increases from 0.01 M to 0.05 M Particle size of the doped powder does not vary too much from the undoped one which shows that 10 mol% Gd_2O_3 does not affect the solubility of the ZrOCl_2 in the alcohol water system Gd_2O_3 doped zirconia nano powders with very high surface area ($300 \text{ m}^2/\text{gm}$) have been prepared from ZrOCl_2 concentration of 0.01 M

One step heat treatment of alcohol water salt solution produces hydrous zirconia particles with a relatively narrow size distribution Two step heat treatment of the precursor solution has been used to prepare hydrous zirconia particle with a still narrower size distribution A microwave treatment at 80% power for 5 seconds and then aging at 50°C for 8 hours seems to be the optimum condition for obtaining hydrous zirconia

particles with narrower width (15 nm) Hydrous zirconia particles with narrow size distribution can also be prepared by heating at 80% and 100 % microwave power for 10 and 15 seconds respectively and subsequent aging at 50 °C but in those cases the particle width increases rapidly with increase in aging time

The variation in the zeta potential of 10 mol% Gd_2O_3 doped zirconia powder was measured as a function of pH and the isoelectric point of the powder was found to be 4.8. The surface properties of zirconia nano particles were modified by coating with silica using a sol gel technique. Time dependent growth of a silica layer on zirconia particles suspended in TEOS sol was measured by observing the changes in zeta potential of zirconia particles. At the initial stage (time $t=0$) the zeta potential of the particles show a high positive value close to the value of zeta potential of pure Gd_2O_3 doped zirconia at that pH. With time the zeta potential value gets decreased and becomes zero at 14.5 hours then negative with increase in aging time. At 27.5 hours it shows a negative value of zeta potential that is close to the zeta potential of silica at that pH.

Introduction of particles of second phase can significantly increase the toughness of a thick film obtained by sol gel method and thereby enhance its resistance to crack growth and propagation during heat treatment. A well dispersed suspension of ZrO_2 or Al_2O_3 particles were added to a polymeric silica solution (TEOS sol). TEOS sol was sufficiently (0.5 day, 1 day, 2 days) aged so that different polymeric structures of SiO_2 can be formed and then the second phase particles were added to the aged sol. A surfactant hydroxyl propyl cellulose (HPC) was used in different amounts (0.002×10^{-3} gm/cc to 0.008×10^{-3} gm/cc) to disperse the second phase particles in isopropanol. These second phase particles interact with polymeric SiO_2 network to form different kinds of flocs, clusters.

chains in the gel. At a HPC concentration of 0.008×10^{-3} gm/cc some chain and ring like arrangements were found in the gel matrix but for other concentrations no regular arrangements of flocs and clusters were found. The distribution of particles in the gel network seemed to be unpredictable and no clear correlation was found between various parameters used for the processing. The gel matrix is severely cracked where there is no second phase particles but the presence of second phase particles in the form of flocs, clusters and chains in the gel matrix holds the film together and in those portions of the film no crack was observed. Thus the second phase particles act as a toughening agent by arresting the crack growth and restrict its propagation in the thick film derived by sol gel technique.

The crystallization of the as prepared amorphous hydrous zirconia particles is studied by calcination at 600°C and 900°C respectively. The undoped crystallized powders prepared from lower precursor ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) concentration show only cubic phase whereas the powders with higher particle size prepared from higher amount of precursor concentration show a mixture of cubic and monoclinic phases at 600°C . However for Gd_2O_3 doped powder it is only cubic phase that exists in the crystallized powders in the temperature range from 600°C to 900°C and the primary crystallite size proved to be independent of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration.

In Conclusion

1. The particle size of undoped and Gd_2O_3 doped zirconia powder does not vary much if other parameters are kept constant.

- 2 Hydrous zirconia powders with particle size down to 40 nm were successfully prepared. The particle size could be varied by varying the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ concentration.
- 3 The high BET surface area of the dried powders suggests that a dried particle of hydrous zirconia consists of many elementary particles. The particle size obtained from BET surface area is 6 nm, whereas it is 8 nm from x-ray line broadening for powders prepared from a precursor concentration of 0.01 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$.
- 4 Hydrous zirconia particle with narrower size distribution (15 nm width) can be produced by two-step heat treatment of the precursor solution.
- 5 The isoelectric point of 10 mol% Gd_2O_3 doped zirconia is found to be 4.8.
- 6 The surface characteristics of Gd_2O_3 doped zirconia nano powders can be modified by coating with a second phase particle using sol-gel method.
- 7 A composite film between 0.25 μm to 0.5 μm in a single coating can be prepared by strengthening it with second phase particulate matter by sol-gel technique.

APPENDIX 1

STEPS IN THE MEASUREMENT BY HPPS

- 1 First the instrument is switched on and the temperature is allowed to stabilize for 30 minutes
- 2 Then HPPS software is started. It is to be noted that after switching on the software should not be started until the unit beeps twice. If this is not done then the software will not connect the optical unit.
- 3 The sample is prepared well (i.e. in well dispersed condition) and the cuvette is filled with the sample upto 10 mm of its height (the maximum height upto which it can be filled should not exceed 15 mm).
- 4 The cuvette is placed in the sample holder delicately and the lid is closed. Then the temperature is allowed to reach the desired temperature.
- 5 A new measurement database is created or opened and *manual measurement* is started by selecting *Measure-Manual*.
- 6 Then 'start' button is pressed and the instrument starts to take the measurement.

APPENDIX 2

CALCULATION OF PARTICLE SIZE FROM PHOTOGRAPH

The particle size is calculated from the photograph developed from the negative by using the following formula

The particle size ϕ is given by

$$\phi = \frac{S \times 4}{M \times m}$$

S = particle size on photograph developed from the negative

ϕ = actual size of the particle

M = Magnification at the TEM screen

m = magnification by which the negative is magnified into a picture

In the present calculation the value of m is maintained 4.3 in every cases (except for nucleation and growth experiment in this case value of m was taken as 4.7)

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